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OSCILLOGRAPHIC POLAROGRAPHY

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In the last few years a number of articles has appeared [1] which have been devoted to the study of reduction processes of certain ions on the dropping mercury cathode by means of oscillographic polarography.

While in ordinary polarography the e.m.f. is applied to the electrolyzer fairly slowly, at the rate of about 0.005 V per second, so that one is unable to study rapid processes, it is possible, by the use of oscillographic polarography, to attain a very rapid rate of voltage application to the cell of up to 10^2 V per second and higher.

This enables many chemical processes occurring on the dropping mercury electrode to be studied from different aspects.

We constructed an oscillographic polarograph, the general appearance of which is illustrated in Fig. 1 (see plate, page 363), where I is the oscillographic polarograph; II is the electronic oscillograph; III is a vacuum tube voltmeter; IV is a voltmeter or potentiometer; and V is the electrolytic cell, consisting of a dropping mercury cathode and a saturated calomel electrode (the electrolytic cell is screened in order to prevent interference with the oscillographic curve.

The set-up used is shown schematically in Fig. 2.

1. Description of the Oscillographic Polarograph. A saw-tooth wave voltage generator feeds the horizontal deflecting plates 1 and 2 of the oscillograph. This saw-tooth voltage with a given voltage amplitude regulated by a voltage amplifier is applied to the electrolyzer electrodes, which are connected in series with a resistance box. As a result of the application of a definite voltage to the polarographic cell containing the test solution, a current develops. After amplification, this current is applied to the vertical deflecting plates 3 and 4. With this set-up, the horizontal deflection is proportional to the voltage applied

to the polarographic cell, while the vertical deflection is proportional to the current flowing through the polarographic cell.

It is known that by changing the value of the voltage applied to the cell containing the test solution, it is possible to observe the beginning of the reduction or oxidation of an ion on the dropping mercury cathode by the sharp change in the value of the current passing through the cell.

Knowing the value of the voltage at which reduction or oxidation of an ion starts on the dropping mercury cathode, it is possible to detect a particular chemical element in solution.

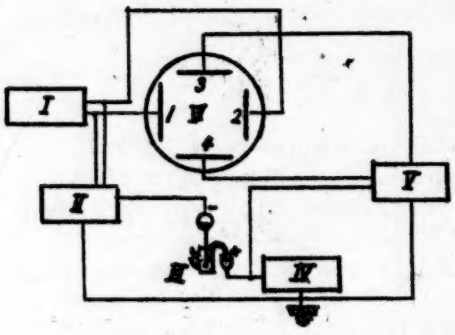

Fig. 2. Schematic diagram of the oscillographic polarograph:
I – Saw-tooth wave voltage generator;
II – voltage amplifier;
III – cell;
IV – resistance box;
V – current amplifier;
VI – oscillograph

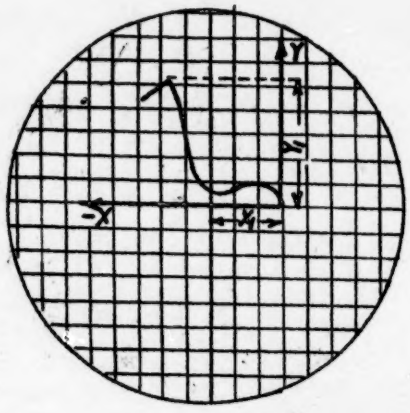

Fig. 3. An oscillographic curve for lead.

A further increase in the voltage applied to the electrolytic cell after attaining the reduction or oxidation potential for a particular ion leads to an increase in the current passing through the electrolytic cell to a certain maximum value. From this maximal peak current passing through the cell, it is possible to determine the concentration of the test ion in solution.

The oscillographic polarograph which we built gave oscillograms (Fig. 3) where the voltage applied to the cell lies along the abscissa, while the values of the current passing through the polarograph cell lie along the ordinate. Coordinates (x_1, y_1) characterize a particular element and its concentration in solution.

For determination of the concentration of a test ion, only the largest

curve which depicts the reduction or oxidation of the ion on one drop of mercury with a maximum area (this corresponds to the point of detachment of the drop from the capillary) is taken into consideration.

In constructing this oscillographic polarograph several modifications were made of the set-up proposed by Delahay [2].

The radio-technical set-up consists of several stages with different functions: 1) a saw-tooth wave voltage generator; 2) an amplifier for the saw-tooth wave voltage applied to the electrolyzer; 3) an amplifier for the current passing through the polarographic cell; 4) a supply source (for anode voltage and filament heating).

Essential modifications were made to the saw-tooth voltage amplifier and the current amplifier, respectively, in order to increase the sensitivity.

The Saw-tooth Voltage Generator. The generator supplies a saw-tooth voltage (Fig. 4) with an amplitude up to 200 V. The frequency of the oscillations generated can be changed from 1 to 50 cycles. With such a frequency it is possible to change the time taken for the voltage to grow to its maximum from 1 to 1/50 second. A time of 1/50 second between two successive voltage peaks overlaps the time necessary for the ion reduced on a drop to be oxidized again.

The most suitable operating frequency in the case of saw-tooth voltages is from 5 to 20 sweeps/second.

The saw-tooth voltage depicted in Fig. 4 is applied directly from the generator to the horizontal deflecting plates. The frequency of the saw-tooth oscillations of the generator can be measured if it is applied to the horizontal deflecting plates, while at the same time an alternating voltage with a period of 50 cycles is applied to the vertical deflecting plates from the circuit. The generator frequency will then be $n=50/n$,[1] where n is the number of sweeps observed on the oscillograph screen.

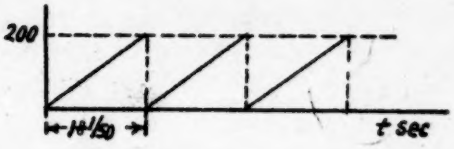

Fig. 4. Saw-tooth voltage with an amplitude of up to 200 V.

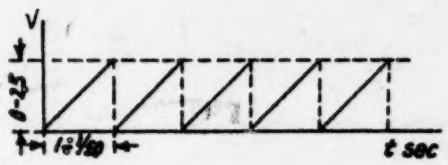

Fig. 5. Amplitude value of the saw-tooth voltage from 0 to 2.5 V.

Voltage Amplifier. The saw-tooth voltage amplifier is capable of applying a saw-tooth voltage with an amplitude of 0 to 2.5 V to the cell (Fig. 5).

For any chemical element in the test solution, therefore, it is possible to select a particular voltage for applying to the cell such that the element is reduced on the dropping mercury cathode.

The magnitude of the saw-tooth voltage can be measured with a vacuum tube voltmeter or potentiometrically (the voltmeter or potentiometer is connected to the electrodes of the polarographic cell):

$$V_{\sim} = 2(V_{meas.} - V_{=}), \qquad (1)$$

[1] In subsequent experiments we used a mechanical counter which registered the number of sweeps/unit time for determining the frequency of the saw-tooth generator vibrations.

where $V_{\sim}$ is the value of the saw-tooth voltage applied to the cell; $V_{=}$ the value of the negative constant voltage applied to the cell and $V_{meas.}$ the value measured potentiometrically or by means of a vacuum tube voltmeter.

In order to avoid distortions introduced by interference, measurements were made before registering the oscillogram.

Current Amplifier. The current amplifier is designed for increasing the weak currents developed in the cell to a value which can be registered by the oscillogram.

Its operating conditions are sensitive to electromagnetic interference and to the micro-background effect (particularly for low concentrations and currents). These are removed by screening and damping the current amplifier.

Supply Source. A suitable source of anode supply for this particular set-up is one provided by an electronic voltage stabilizer for 60-80 mA. Filament heating is supplied by an accumulator.

In order to avoid distortion the anode supply source is placed at some distance from the polarographic cell.

II. A Consideration of the Oscillograms Obtained During the Reduction of Certain Ions on the Dropping Mercury Cathode.

As examples of the sort of polarograms obtained we adduce Figs. 6 and 7 for solutions of 10^{-4} M $CdCl_2$ and 10^{-4} M $ZnCl_2$ in N KCl.

Electrolysis was carried out using a saw-tooth voltage of amplitude 1.8 V in the presence of dissolved atmospheric oxygen. Fig. 6 shows a number of oscillographic curves obtained for one drop of mercury during its growth, while Fig.7 shows the maximal curve for one mercury drop.

The first maximum on the right corresponds to the maximum capacity current. The second maximum is the result of the reduction of cadmium ions, while the third and fourth maxima correspond to zinc reduction on the dropping mercury cathode. The fourth maximum is small compared with the third. This is clearly shown in Fig. 7.

The oscillographic waves of cadmium and zinc whose appearance at -1.12 and -0.60 V relative to the saturated calomel electrode are clearly defined and can be measured accurately. The fourth maximum on the curve is caused by dissolved atmospheric oxygen.

In order to determine the effect of dissolved atmospheric oxygen on the reduction of cadmium and zinc ions (on the dropping mercury electrode) we electolyzed the same solutions after removal of dissolved oxygen, using the same value for the amplitude of the saw-tooth voltage as before.

Fig. 8 shows what happens during the life of a drop. We can clearly see the oscillographic waves for cadmium and zinc. When the curves on Figs. 6 and 8 are compared, it is not difficult to see that oxygen affects the zinc reduction to a greater extent than the cadmium reduction. In test solutions free from dissolved oxygen the second zinc maximum disappears.

Fig. 9 shows a polarogram for one maximal curve of the mercury drop, where we can distinctly see waves for cadmium and zinc which appear on the curve at potentials equal to those which are characteristic of cadmium and zinc in normal polarography.

The oscillograms in Figs. 10 and 11 are for 0.1 N potassium chloride containing $2 \cdot 10^{-5}$ M $CdCl_2$ and $1.9 \cdot 10^{-5}$ M $ZnCl_2$. Electrolysis was carried out in the presence of dissolved atmospheric oxygen at the same saw-tooth voltage amplitude used before.

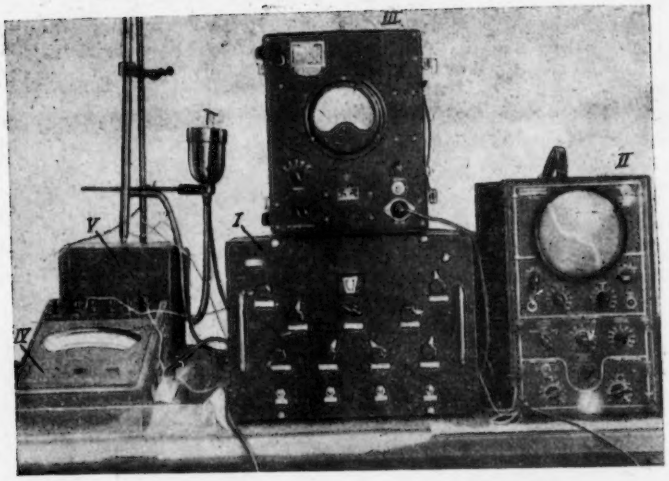

Fig. 1. General appearance of the oscillographic polarograph.

Fig. 6. Oscillographic curves for Cd^{2+} and Zn^{2+} for one drop during its growth; m = 2.6 mg/sec, t = 3.5 sec, v = 18 V/sec.

Fig. 7. Oscillographic curve for Cd^{2+} and Zn^{2+} for a maximal cross-sectional area of the mercury; m = 2.6 mg/sec, t = 3.5 sec, v = 18V/sec.

Fig. 8. Oscillographic curves for cadmium and zinc on 1 drop of mercury during its growth; m = 2.6 mg/sec, t = 3.6 sec, v = 18V/sec.

Fig. 9. Oscillographic curves for cadmium and zinc on 1 drop of mercury at its maximal cross-sectional area; m = 2.6 mg/sec, t = 3.5 sec, v = 18 V/sec.

Fig. 10. Oscillographic curves for cadmium and zinc on 1 drop of mercury during its growth; m = 2.6 mg/sec, t = 3.5 sec, v = 18 V/sec.

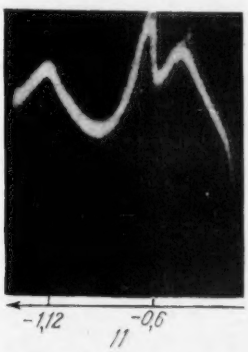

Fig. 11. Oscillographic curve for cadmium and zinc on 1 drop of mercury at its maximal cross-sectional area, m = 2.6 mg/ t = 3.5 sec, v = 18 V/sec

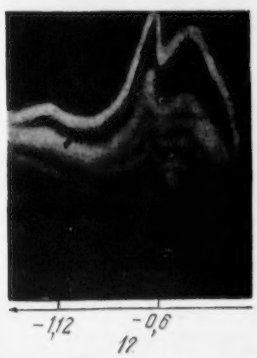

Fig. 12. Oscillographic curves for cadmium and zinc on 1 drop of mercury during its growth, m = 2.6 mg/sec, t = 3.5 sec, v = 18V/sec.

Fig. 13. Oscillographic curves for cadmium and zinc for 1 drop of mercury at its maximal cross-sectional area; m = 2.6 mg/sec., t = 3.5 sec, v = 18 V/sec.

Fig. 10 shows what happens during the life of a drop. Though the concentration of the test ions in solution was five times less than in the previous experiments, the cadmium and zinc waves are still well defined.

Fig. 11 is a maximal curve. After removal of oxygen from the 0.1 N KCl containing $2 \cdot 10^{-5}$ M $CdCl_2$ and $1.9 \cdot 10^{-5}$ M $ZnCl_2$, the values for the maximal zinc and cadmium currents are less than the corresponding maximal values in solutions containing atmospheric oxygen (See Figs. 12 and 13).

Figs. 12 and 13 show that dissolved oxygen has a greater effect on the reduction of zinc than on the reduction of cadmium (compare Figs. 11 and 13). In the absence of oxygen, the strict linear relation between the test ion concentration and the value of its maximal current is still maintained when the rate of change of potential remains constant during the experiment. Since the rate of change of the saw-tooth voltage applied to the electrolytic cell has an appreciable effect on the height of the maximal curve of the test ions we carried out a number of experiments in order to study this effect.

Effect of the Rate of Potential Change on the Value of the Maximal Current of the Reduced Ion.

The rate of change of the applied potential depends on the frequency of the generator (ν) and on the amplitude of the saw-tooth voltage ($V\sim$). The product of these two quantities gives the rate of change of the saw-tooth potential applied to the electrolytic cell.

10^{-4} M $CdCl_2$ in 0.1 N KCl and 10^{-4} M $ZnCl_2$ in 0.1 KCl, respectively, were tested in the absence of atmospheric oxygen at various rates of potential change. Electrolysis was carried out using two dropping mercury electrodes with different drop times. Randles [3], derived an equation for the maximal value of the ocsillographic wave when a dropping mercury cathode is used; it is of the following form:

$$I_{max} = \frac{1.24\pi F}{(0.0118)^{1/2} 10^3} n^{3/2} \gamma^{2/3} t^{2/3} \underline{v}^{1/2} D^{1/2} c, \qquad (2)$$

where I_{max} is the maximal current of the oscillographic wave expressed in amperes; F - the Faraday number; $\underline{n}$ - the number of electrons participating in the reaction; γ is related to the expression $r_0^3 = \frac{3mt}{4\pi d} = \gamma t$, i.e., $\gamma = \frac{3m}{4\pi d}$ (where $\underline{m}$ is the amount of mercury in grams issuing from the capillary in 1 second; $\underline{d}$ - the density of mercury; $\underline{t}$ - the drop time); $\underline{v}$ - the rate of change of potential in volts per second; D - the diffusion coefficient of the reduced ion; and $\underline{c}$ - the ionic concentration expressed in mols per liter.

We calculated the maximal current by means of equation (2) and compared the results with the experimental results. They are adduced in Table 1.

The table shows that the experimental results do not agree with the calculated ones. For reductions of Cd^{2+} on a dropping mercury cathode, the deviation between calculated and experimental values is as much as 21%, and this deviation increases with increasing rate of potential change.

Since the zinc ion is reduced irreversibly on the dropping mercury cathode, the percentage deviation between experimental and calculated is considerably greater.

This deviation of the experimental values from those calculated by means of Randles' equation is a consequence of the fact that Randles derived his equation for the maximal current on the basis of a differential equation for linear diffusion, instead of an equation for convective diffusion to the surface of the expanding drop.

TABLE 1

The Effect of the Rate of Potential Change on the Value of the Maximal Current of the Reduced Ion

Amplitude of the saw-tooth voltage, in volts. ($V_{\sim}$)	Frequency of the saw-tooth voltage generator (ν)	Rate of change of voltage, in volts (v)	Maximal current of the reduced ion		Difference in % between calculated and experimental values [1]
			Found μA	Calculated from (2) μA	
10^{-4} M $CdCl_2$ in 0.1 N KCl; $D_{Cd^{2+}} = 0.52 \cdot 10$ cm^2/sec; m = 2.18 mg/sec; t = 3.5 sec; h = 280 mm					
-1.22	1.25	1.53	5.81	7.25	~19.9
-1.22	2.27	2.77	7.80	9.75	~20.0
-1.22	6.25	7.63	12.7	16.18	~21.5
-1.22	7.16	8.74	13.7	17.32	~21.0
10^{-4} M $CdCl_2$ in 0.1 N KCl; m = 0.76 mg/sec; t = 8.28 sec; h = 470 mm					
-1.1	3.0	3.3	7.50	9.35	~19.8
-1.00	6.2	6.2	10.0	12.83	~22.0
-1.00	8.3	8.3	11.24	14.84	~24.2
-0.86	10.0	8.6	11.8	15.11	~21.8
-0.98	16.6	~16.3	16.2	20.81	~22.0
10^{-4} M $ZnCl_2$ in 0.1 N KCl; $D_{Zn^{2+}} = 0.5 \cdot 10^{-5}$ cm^2/sec; m = 0.76 mg/sec; t = 6.4 sec; h = 470 mm					
-1.66	3.57	5.93	6.54	10.36	36.9
-1.58	7.10	~11.22	8.66	14.24	39.2
-1.62	10.00	16.2	10.30	17.13	39.8
-1.44	12.50	18.0	10.71	18.06	40.7
-1.66	16.60	27.56	11.8	22.34	47.2

1) The calculated values are taken as 100%.

Moreover, in deriving his equation Randles postulated that the concentration of the test ion in solution is equal to the concentration of the same ion near the surface of the mercury drop plus the product of the metal concentration in the mercury amalgam and the square root of the ratio of the diffusion coefficient of the metal in the amalgam to the diffusion coefficient of the ion in solution. This postulate cannot be accepted since the condition of diffusion to the dropping mercury electrode differs considerably from the conditions assumed by Randles.

From Table 1 it follows that with an increasing rate of saw-tooth voltage change the maximal current of the reduced ion increases. In carrying out quantitative analysis, therefore, the rate of voltage change must be standardized.

Effect of the Amplitude of the Saw-tooth Voltage on the Dropping Period of the Mercury Electrode.

It is known that when a negative potential is applied to a cell the drop time (t) of the mercury electrode changes according to the electrocapillary curve. We were interested in comparing the changes in dropping time for various saw-tooth

voltages with t obtained on applying a fixed negative potential. A number of experiments were therefore carried out to give results which are shown graphically in Fig. 14. In all cases electrolysis was carried out in the absence of atmospheric oxygen.

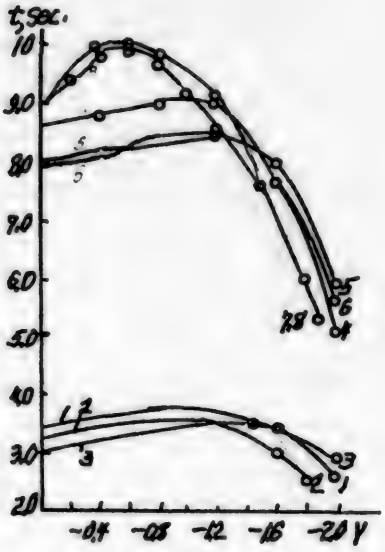

Fig. 14. Change in drop time of the mercury with the amplitude of the saw-tooth voltage.

The amplitude of the saw-tooth voltage and the drop time in seconds (t) are plotted along the abscissa and ordinate respectively. Curves 1,2 and 3 Fig. 14 represent electrocapillary curves obtained in 0.1 N KCl, $5 \cdot 10^{-4}$ M $CdCl_2$ in 0.1 N KCl and $5 \cdot 10^{-4}$ M $CdCl_2$ + $5 \cdot 10^{-4}$ M $ZnCl_2$ in 0.1 N KCl.

On comparing these curves it is not difficult to observe that the electrocapillary curve for 0.1 N KCl is higher than curves 2 and 3. The elctrocapillary maximum is shifted to more negative values of the saw-tooth voltage in all cases. Considerable changes in the drop time are observed beginning with a saw-tooth voltage amplitude of 1.2 V relative to the saturated calomel electrode. Curves 4,5,6,7, and 8 were obtained with a slow drop time. Curves 4, 5, and 6 correspond to electrocapillary curves obtained in 0.1 N KCl, 10^{-4} M $CdCl_2$ in 0.1 M KCl and 10^{-4} M $ZnCl_2$ in 0.1 N KCl, respectively. Curves 7 and 8 were obtained in 0.1 N KCl and 10^{-4} M $CdCl_2$ in 0.1 N KCl on applying a constant negative potential to the cell.

A comparison of these curves shows that curves 7 and 8 are somewhat higher than curves 4 and 5, while the electrocapillary maxima on curves 7 and 8 are located at a negative potential of -0.56 V relative to the saturated calomel electrode, while the maxima in 5 and 6 are displaced to even more negative values of $V_{..}$.

When electrolysis is carried out using a slow drop time, the changes in the drop time which begin at $V_{..}$ = 1.2 V are considerably greater than in the case of a capillary with a drop time of ca. 3 sec. (compare curves 4,5, and 6 with curves 1, 2, and 3, Fig. 14).

Since the amplitude of the saw-tooth voltage does effect the drop time, it is necessary (when taking oscillograms) in carrying out quantitative analysis to specify the drop time at a given value of the applied voltage $V_{..}$.

Quantitative Determination of Certain Ions.

Since it has been shown that the rate of change of the saw-tooth voltage and the effective pressure on the dropping mercury affect the value of the maximal current of the reduced ion, we used steady values for v and for the pressure on the dropping mercury. Electrolysis was carried out in the absence of atmospheric oxygen. The results are given in Tables 2, 3, 4, and 5.

TABLE 2

Maximal current values for various cadmium concentrations in 0.1 N KCl
m = 2.6 mg/sec; t = 3.5 sec; ν = 10 sweeps/second; $\underline{v}$ = 18 V/sec;
h = 280 mm

Cadmium concentration in mols/liter	Maximal current in μA
10^{-3}	223.0
$5 \cdot 10^{-4}$	115.0
10^{-4}	23.0
$5 \cdot 10^{-5}$	11.7
10^{-5}	2.42
$5 \cdot 10^{-6}$	1.38
10^{-6}	0.31

TABLE 3

Maximal current values for various cadmium concentrations in 0.1 N KCl
m = 0.76 mg/sec; t = 8.28 sec; ν = 7.5 sweeps/second; $\underline{v}$ = 13.77 V/sec;
h = 470 mm

Cadmium concentration in mols/liter	Maximal current in μA
10^{-4}	19.1
$5 \cdot 10^{-5}$	9.75
10^{-5}	2.04
$5 \cdot 10^{-6}$	1.08
10^{-6}	0.24

It is clear from Table 2 that there is a linear relation between maximal current and cadmium concentration. There is a slight deviation from linearity when the solutions are very dilute.

The sensitivity of the oscillographic method is considerably higher than that of the ordinary polarographic method, since the latter can only determine 10^{-5} M $CdCl_2$ even when multi-capillary electrodes are used. An ordinary polarogram for 0.1 N KCl containing 10^{-5} M $CdCl_2$ is shown in Fig. 15 as an example. Two capillaries with differing drop times were used to get this curve. The volume of the test solution was 25 ml. A cadmium wave is clearly discernible on this curve but the limiting current of the cadmium has only a small plateau. Following after the cadmium curve there is an appreciable supplementary current which is caused by the tangential movement of the mercury surface and by the shearing off of drops.

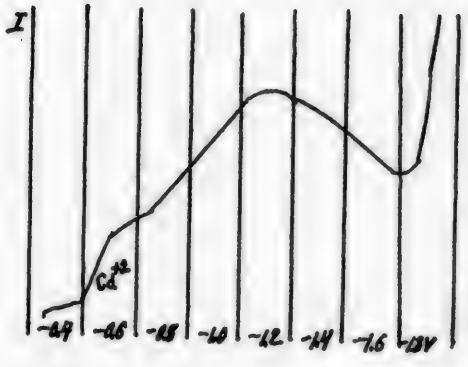

Fig. 15. Polarogram for cadmium chloride in 0.1 N KCl.

On halving the cadmium concentration of the last experiment a clear-cut wave for cadmium is no longer discernible since it fuses into the supplementary current. It is not possible therefore to determine concentrations of cadmium of the order of $5 \cdot 10^{-6}$ M $CdCl_2$ by ordinary polarography even when using a multi-capillary set-up. By the oscillographic method, however, it is possible to get a reduction curve for cadmium on the screen even for a concentration of 10^{-7} M $CdCl_2$ in 0.1 N KCl.

Table 3 contains results for the maximal current obtained with a slow drop time.

These results show that when a slow drop time is used, there is linear relation between the concentration of the reduced ion and its maximal current.

Table 4 contains results for zinc.

TABLE 4

Maximal current values for various concentrations of zinc in 0.1 N KCl m = 2.6 mg/sec; t = 3.2 sec; ν = 10 sweeps/second; $\underline{v}$ = 18 V/second; h = 280 mm

Zinc concentration in mols/liter	Maximal current in μA
10^{-3}	235.0
$5 \cdot 10^{-4}$	120.0
10^{-4}	24.0
$5 \cdot 10^{-5}$	12.4
10^{-5}	2.61
$5 \cdot 10^{-6}$	1.46
10^{-6}	0.35

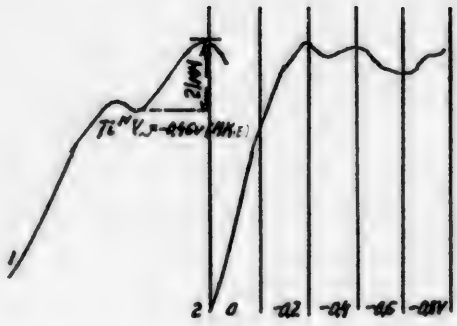

Fig. 16. Oscillogram and polarogram for Ti(IV) in the presence of iron and vanadium.

The results in Table 4 show that there is a linear relation between maximal current and zinc concentration; the curve deviates slightly from linearity on going toward low concentrations. The maximal current for zinc is somewhat higher than that of cadmium (compare the results of Tables 2 and 4).

Results given in Table 5 illustrate the effect of one ion on the maximal current of another when both are present together in 0.1 N KCl Solution.

TABLE 5

Maximal Current for Various Concentrations of Cadmium and Zinc in 0.1 N KCl

m = 2.6 mg/sec; t = 3.2 sec; ν = 10 sweeps/second; $\underline{v}$ = 18 V/sec; h = 280 mm;

$$\frac{c_{Cd}}{c_{Zn}} = 1$$

Concentration of cadmium and zinc in mols/liter	Maximal current in μA	
	Cadmium	Zinc
10^{-3}	250.2	163.8
$5 \cdot 10^{-4}$	126.8	84.48
10^{-4}	25.92	17.55
$5 \cdot 10^{-5}$	13.48	9.15
10^{-5}	2.73	1.92

It follows from Table 5 that when zinc and cadmium both occur simultaneously in a test solution the linear relation between concentration and maximal current for both Cd^{2+} and Zn^{2+}, respectively, is maintained within the limits of the experimental error of ordinary polarography. A comparison of the results given in Tables 2, 4, and 5 shows that the zinc ion increases the value of the cadmium maximal current to a value greater than that obtained, I_{max}, when Zn^{2+} is absent. The cadmium ion decreases the maximal zinc current to a value less than I_{max} when cadmium is absent.

Fig. 8 represents an oscillogram obtained when both cadmium and zinc ions were present together in solution. The maximal current of Cd^{2+} is considerably greater than the maximal Zn^{2+} current. The results in Table 5 show that the oscillographic method is a suitable one for investigating the effect of one ion on another as well as for the quantitative analysis of dissolved substances.

As an example of the superiority of the oscillographic polarograph over the ordinary polarograph we have adduced the results of an experiment on the determination of quadrivalent titanium in the presence of trivalent iron and quinquevalent vanadium.

The two curves given in Fig. 16 were obtained in 1 N H_2SO_4 saturated with sodium oxalate; 1 ml of solution contained 10 γ Ti(IV), 100 γ V(V) and 250 γ Fe^{3+}. The first curve is an oscillographic curve on which a titanium wave is clearly defined, while no titanium wave can be observed on the second curve, which was obtained by means of ordinary polarography; in the latter case the titanium wave has fused into the wave of trivalent iron and quinquevalent vanadium. On Fig. 16 $V_{\sim}$ is the amplitude of the saw-tooth voltage at which titanium is reduced on the dropping mercury cathode.

SUMMARY

1. A first model of an oscillographic polarograph has been constructed by means of which microanalysis of solutions can be carried out.

2. The effect of the rate of potential change on the value of the maximal current of the reduced ion has been studied.

3. The effect of the amplitude of the saw-tooth voltage on the drop time of the mercury electrode has been studied.

4. It has been shown that the linear relation between the value of the maximal current of a reduced ion and its concentration in solution only holds when the rate of potential change and the effective pressure on the dropping mercury remain constant.

5. It has been shown that by means of the oscillographic polarograph constructed it is possible to determine a test ion in concentrations of 10^{-8} mol/liter.

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THE APPLICATION OF COMPLEXONES IN POLAROGRAPHY

1. DETERMINATION OF TITANIUM

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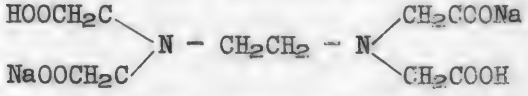
Zeltzer [1], has shown that titanium (IV) gives a reduction wave in weak acid solution at a potential of -0.81 V relative to the saturated calomel electrode. This wave is the result of the process Ti (IV) + e → Ti(III).

Nevertheless, according to the results of other investigators [2], as well as ourselves, the Ti (IV) wave obtained in acid solution is poorly defined and is not suitable for quantitative determination of titanium. This is the result chiefly of the irreversibility of the process as shown by Strubl [2], (because the oxidation of titanium (III) occurs at a potential of -0.18 V) and the rather extended wave obtained fuses with the hydrogen ion wave. Complexing agents are therefore used for the polarographic determination of titanium. It has been shown that by complexing Ti (IV) with tartrate, citrate [2], thiocyanate [3], and oxalate [4], clearly defined waves are obtained which correspond to the reversible process Ti (IV) $\rightleftharpoons$ Ti (III), during which the reduction potential if shifted to more positive values. E.g., for tartaric acid and citric acid this potential is -0.48 V.

Zanko and co-workers developed a method of determining titanium in bauxite, kaolin, slags, [5], casts and steels [6] in which tartaric acid was used as a complexing agent; he showed that for the determination of titanium in casts and steels in 14% tartaric acid solution, after preliminary reduction of iron (III) with aluminum dust, the method which is based on a calculating technique has an error of 4-5% for a titanium content of 0.4 - 1%. A 1 M tartaric acid solution in 0.5 M sulfuric acid has also been used for polarographic determination of titanium in clays, granites, syenites and other minerals and in ores [7]. In this solution the half-wave potential is -0.3 V against the saturated calomel electrode.

Under these conditions titanium can be determined in the presence of Al, Zr, Th, Nb, Ta, the alkali and the alkaline earth elements. Fe, Cu, and Cr are precipitated first on the mercury cathode. Only uranium interferes. Titanium has been determined in clays [4], using sodium oxalate in 1 N sulfuric acid as supporting electrolyte, the solution also contains 8% urea for maximum suppression. According to the author iron does not interfere under these conditions. It has been shown [8], that the half-wave potential of titanium in this supporting electrolyte does not depend on the concentration of titanium and iron.

We used Trilon B which is the disodium salt of ethylenediaminetetracetic acid as the complexing agent for the polarographic determination of titanium



Trilon B is also know as "Complexone III", "Versene" etc.

This reagent forms very stable complexes with many metals and is finding ever increasing application in chemical analysis for the determination of many metals [9].

Trilon B is a white crystalline material which is comparatively soluble in water but practically insoluble in acids. According to our observations the salt hardly dissolves at all at a pH of ca. 2.

Complexones have hitherto only found limited application in polarography; nevertheless the fact that they form complexes which strongly displace the reduction potentials of many metals, may open up many new possibilities for the determination of metals when these are present simultaneously.

E.g., is has been shown that by using Complexone III it is possible to determine cobalt in the presence of nickel and other metals, if the cobalt is first of all oxidized to Co(III), and also to determine iron in the presence of a large excess of copper [10].

Polarographic methods involving the use of Complexone III have also been suggested for the determination of thallium in the presence of lead and tin [11], molybdenum in the presence of tungsten [12], and uranium in the presence of chromium, titanium, etc., [13].

The effect of pH on the displacement of the reduction or oxidation potentials of the complexes of several cations with Complexone III has been investigated [14].

EXPERIMENTAL

Measurements were made with a Heyrovsky automatic-registering polarograph with a galvonometer sensitivity of 2.21×10^{-9} A/mm. The electrolyzer was connected to a saturated calomel electrode serving as anode by means of an agar-agar bridge. All the potentials given in this article are relative to the saturated calomel electrode.

The capillary had the following characteristics $m^{2/3} t^{1/6} = 1.434$ $mg^{2/3}$ $sec^{-1/2}$ in a 1 N solution of KCl-0.05 N HCl at -0.8 V. The cell was thermostated at 25 ± 0.5°. pH's were measured with an LP-4 vacuum tube voltmeter and universal indicator (for coarser measurements).

The following solutions were used:

1. A stock solution of titanium sulfate was prepared by treating potassium fluorotitanate three times in succession with sulfuric acid with heating till evolution of sulfuric acid vapors. The cooled solution was made up to standard volume with water. The titanium content of the solution was determine gravimetrically as TiO_2 after precipitation with ammonia. 1 liter contained 1.8682 g TiO_2. Solutions of lower concentration were made from the stock solution by dilution with 5% sulfuric acid.

2. 0.3 M solutions of Trilon B in water or 0.1 M in 2 M sodium acetate were prepared after recrystallization of Trilon B from water.

3. A solution of 2 M sodium acetate.

4. Redistilled acids.

The Polarographic Characteristics of the Complex formed between Titanium and Trilon B.

Titanium forms a complex with Trilon B at certain pH's which is reduced on the dropping mercury cathode to give a well defined wave with a half-wave

potential which depends on the pH.

Curves 1 and 2 (Fig. 1) were obtained with a solution which was 1.17 mM with respect to titanium and 0.1 M and 2 M, respectively, with respect to Trilon B and sodium acetate, the pH was ca. 5.

The half-wave potential at this pH was -0.473 V. Analysis of this wave by means of the Heyrovsky-Ilkovich equation

$$E_{c.e.} = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{i_d - i}$$

gave a slope of 0.062 V on constructing a graph; his is in good agreement with the theoretical value of 0.059 for an unielectron process. This indicates that the reduction of the complex titanium ion is reversible and proceeds according to the following scheme

$$Ti\ (IV) + e \rightleftharpoons Ti\ (III).$$

Titanium is also reduced in a solution of sodium acetate (2 M) in the absence of Trilon B to give a wave with a half-wave potential of ca. -1 V; this wave however is extended and does not have a clear-cut plateau for the limiting current (Curve 3, Fig. 1).

Effect of pH on the Titanium Half-Wave Potential.

The effect of pH on the half-wave potential of the titanium complex was also studied. Solutions were prepared which were 0.468 mM, 0.1 M, and 2 M respectively, with respect to titanium, Trilon B, and sodium acetate; the pH was varied.

The pH was altered by addition of either sulfuric acid or ammonia. The results obtained are given in Fig. 2 and Table 1

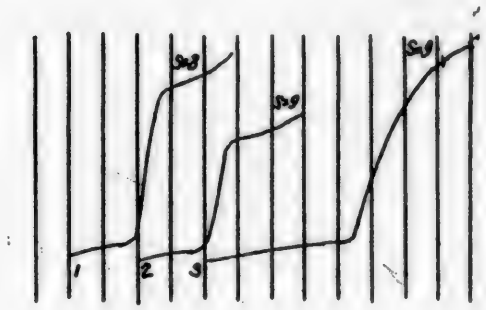


Fig. 1. Curves 1 and 2 - 1.17 mM solution of titanium in a supporting electrolyte of 0.1 M Trilon B and 2 M sodium acetate, pH ca. 5; Curve 3 - 1.17 mM solution of titanium in a supporting electrolyte of 2 M sodium acetate.

TABLE 1

pH of solution	$E_{\frac{1}{2}}$ in V against the saturated calomel electrode.
5.50	- 0.555
4.60	- 0.427
3.40	- 0.418
2.25	- 0.391
0.80	Wave distorted

The results in Table 1 show that the pH has a considerable effect on the half-wave potential of the titanium complex. At low pH's the half-wave potential shifts

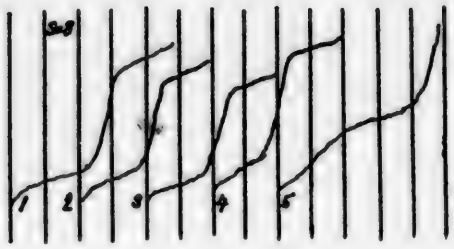


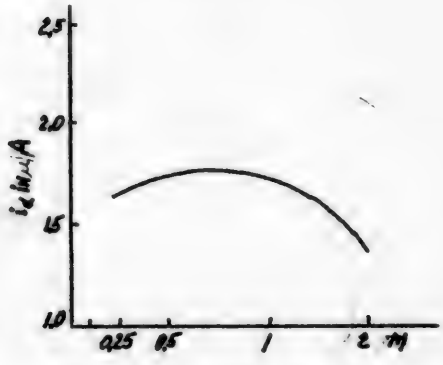
Fig. 2. Effect of pH on the half-wave potential of the titanium complex: 0.468 mM solution of titanium in a supporting electrolyte of 0.1 M Trilon B and 2 M sodium acetate for various pH values: 1) 5.50; 2) 4.60; 3) 3.40; 4) 2.25; 5) 0.80.

to the positive side while at very low PH, the complex decomposes.

This indicates that the stability of the titanium complex decreases with decreasing pH. At high pH's the Trilon B does not protect titanium from hydrolysis and as a consequence no titanium wave is obtained. This agrees with Przhibil's results [9], and indicates that although the complexone strongly inhibits the separation of titanium hydroxide, the latter can be precipitated quantitatively on long standing (ca. 5 hours). For quantitative polarographic determination of titanium, therefore, it is best to use a solution possessing buffer activity as the supporting electrolyte. For this purpose we used a 2 M solution of sodium acetate having a pH of 4.5-5.0.

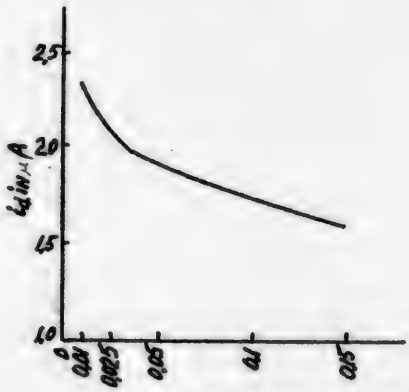
Effect of Sodium Acetate and Trilon B Concentrations, Respectively, on the Half-Wave Potential and on the Value of the Diffusion Current.

During a study of the effect of sodium acetate concentration, it was found that the half-wave potential of the titanium complex hardly changes at all with changes in sodium acetate concentration when the pH was kept constant. The diffusion current decreases slightly with increasing sodium acetate concentration, starting at a concentration of 0.5 N sodium acetate, as shown in Fig. 3 for a 0.468 mM solution of titanium which was also 0.1 M with respect to Trilon B and had various concentrations of sodium acetate. The Trilon B concentration does not affect the half-wave potential of the titanium complex when the pH is kept constant, the diffusion current decreases slightly with increasing Trilon B concentration (Fig. 4).



Sodium Acetate Conc.

Fig. 3. Effect of sodium acetate concentration on the value of the diffusion coefficient of titanium. 0.468 mM of titanium in 0.1 M Trilon B as supporting electrolyte.



Trilon B conc. in M

Fig. 4. Effect of Trilon B concentration on the value of the diffusion current of titanium. 0.468 mM solution of titanium in 0.2 M of sodium acetate as base electrolyte.

All further measurements were therefore made in 2 M sodium acetate which is 0.1 M with respect to Trilon B, since it is obvious from the polarograms obtained under these conditions, that the limiting current is the optimum.

Determination of the Diffusion Current Constant.

The diffusion current constant was determined by carrying out measurements in 2 M sodium acetate which was 0.1 M with respect to Trilon B and containing titanium in concentrations varying from $2.34 \cdot 10^{-4}$ - $2.34 \cdot 10^{-3}$ M, and also in the supporting electrolyte alone. The results obtained are given in Table 2 and Fig. 5.

TABLE 2

Ti taken in mM/l	i_d μA obtained	i_d μA found after correction for residual current.	$K = i_d/c$ μA /mM/liter	Deviation of K, in % of the mean
-	0.238	-	-	-
0.234	0.953	0.715	3.05	-3.93
0.468	1.718	1.480	3.16	-0.31
0.936	3.068	2.830	3.02	-4.75
1.404	4.859	4.621	3.29	+3.93
2.340	8.060	7.822	3.34	+5.09
		Mean . . .	. 3.17 ± 0.11	

These results show that the diffusion current constant varies from 0.31-5% of the mean value which signifies that a linear relation exists between the diffusion current and the concentration of titanium in solution for the concentrations studied, viz. $2.34 \cdot 10^{-4} - 2.34 \cdot 10^{-3}$ M/liter. At high titanium concentrations (ca. 2mM/liter) a maximum is observed on the curve.

Effect of the Order in which Reagents are Added.

We showed that the order in which the reagents are added has an essential effect on the value of the titanium diffusion current. If the sodium acetate is added first to the test solution of titanium, and the Trilon B added subsequently, the diffusion current is lowered considerably. This is the result apparently of the fact that the titanium forms a complex with the sodium acetate which reacts slowly with the Trilon B. This is confirmed by Curve 1, Fig. 6 which was obtained with 0.468 mM of titanium solution when 1 M sodium acetate was added first, followed by Trilon B to 0.05 M.

Curve 2 on the same diagram represents what happens to a solution of the same titanium concentration when the titanium solution is added to a 1 M solution of sodium acetate containing Trilon B at a concentration of 0.05 M. It is necessary, therefore, to use a solution of sodium acetate containing Trilon B as reagent. In this case the order of addition of the reagent is of no significance.

Effect of Iron, Vanadium, Copper and Chromium.

The effect of iron, vanadium, copper and chromium on the polarographic determination of titanium as its complex with Trilon B was investigated. Iron (III) gives a complex with Trilon B in 2 M sodium acetate which is reduced at a potential of -0.12 V, i.e. at a potential which is 0.35 V more positive than

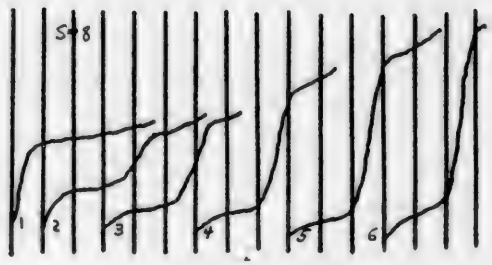


Fig. 5. Polarograms for titanium at different concentrations in a supporting electrolyte of 0.1 M Trilon B in 2 M sodium acetate.

1- Supporting electrolyte; 2- 0.234; 3- 0.468; 4- 0.702; 5- 0.936; 6- 1.170 mM titanium.

the half-wave potential of titanium. Therefore iron in amounts which are 4-5 times that of titanium does not interfere with the titanium diffusion current as is evident from Curves 1 and 2 of Fig. 7. When, however, large amounts of iron are present, exact determination of titanium becomes impossible. The reduction of iron (III) to iron (II) by various reducing agents (hydrazine sulfate, ascorbic acid) leads to a partial reduction of titanium also, both by the reducing agents themselves and by the iron complexes (II) formed, which possess strong reducing powers [15]. When, therefore, large amounts of iron are present, it is necessary to remove it by electrolytic precipitation on a mercury cathode or to separate the titanium by precipitating with ammonia after complexing the iron and titanium with Trilon B. Under these conditions, iron (III) is not precipitated by ammonia, while titanium is precipitated quantitatively on long standing (ca. 5 hours) [9].

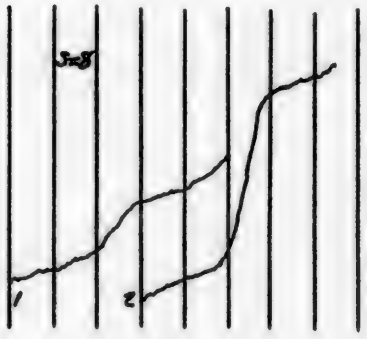


Fig. 6. Effect of the order of addition of the reagents. 0.468 mM of titanium in a supporting electrolyte of 0.05 Trilon B and 2 M sodium acetate.

1- sodium acetate is first added to the titanium solution followed by Trilon B; 2- the titanium is added to sodium acetate containing Trilon B.

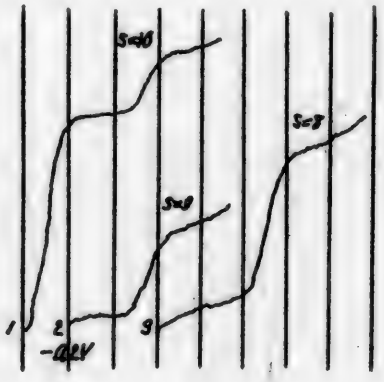


Fig. 7. Effect of iron (III) and chromium (III) on the titanium diffusion current:

1- 22.4 μg of titanium and 75 μg of iron (III) per ml in a supporting electrolyte of 0.1 Trilon B and 2 M sodium acetate; i_d = 1.4 μA; 2- the same solution; polarographing started at 0.2 V; 3- 22.4 μg titanium in 1 ml and 100 μg of chromium (III) in 1 ml, in the same supporting electrolyte; i_d = 1.50 μA.

Vanadium (V) has a considerable effect on the value of the diffusion current of the titanium complex and increases it. On reduction to vanadium (IV) with hydrazine sulfate its effect is not eliminated; vanadium must therefore be removed before determining titanium polarographically.

Copper also interferes since it forms a complex with Trilon B which is reduced on the dropping mercury electrode at a potential near to that for titanium; the half-wave potential of the complex with Cu^{2+} is -0.4 V.

It is essential, therefore, to remove copper as well before determination of titanium with Trilon B. Chromium (III) has practically no effect on the value of the titanium diffusion current (Curve 3, Fig. 7).

Results are given in Table 3 which illustrate the effect of the elements mentioned above, which are of varying valencies, on the diffusion current of the titanium complex with Trilon B.

TABLE 3

Metals taken in μg/ml.						i_d μA found	Observations
Ti(IV)	Fe(III)	Fe(II)	V(V)	V(IV)	Cr(III)		
22.4	-	-	-	-	-	1.48	Fe (III) and V(V) were reduced either by heating with hydrazine sulfate, or with ascorbic acid at room temperature.
44.8	-	-	-	-	-	2.98	
22.4	75.5	-	-	-	-	1.40	
22.4	-	500	-	-	-	1.00	
22.4	-	-	100	-	-	2.17	
44.8	-	-	125	-	-	4.25	
22.4	-	-	-	500	-	7.34	
56.0	-	500	-	250	-	5.00	
22.4	-	-	-	-	50	1.50	
22.4	-	-	-	-	100	1.55	

SUMMARY

1. It has been shown that the complex of titanium with Trilon B is reduced reversibly on the dropping mercury cathode.

2. The effect of pH on the half-wave potential of the complex formed between titantium (IV) and Trilon B has been studied.

3. The effect of the concentrations of Trilon B and sodium acetate on the half-wave potential and the diffusion current of the complex formed between titanium (IV) and Trilon B has been studied.

4. The effect of iron (III) and (II), vanadium (V) and (IV), copper (II), and chromium (III) on the polarographic determination of titanium with Trilon B has been investigate.

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POTENTIOMETRIC TITRATION WITH THE FERRI-FERROCYANIDE ELECTRODE

DETERMINATION OF COPPER

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Of a number of attempts to develop a potentiometric method for copper based on the use of ferrocyanide solutions only two seem to have been successful [1,2].

From published data it is known that the composition of copper ferrocyanide does not correspond to the formula $Cu_2Fe(CN)_6$ but depends on the experimental conditions [1,2,3].

In order to get a precipitate of constant composition the following may be added:

1. A strong electrolyte which is indifferent [3], or which reacts with the ferrocyanide ion [1], or

2. A complexing agent which gives a soluble complex with Cu^{2+} [2].

The combined use of 1 and 2 is also possible [3].

In our opinion the increase in ionic strength in the first case is sufficient to ensure that the activity coefficient of the titrated ion is small enough and remains practically constant during the whole of the titration; this consequently ensures a constant composition for the precipitate.

Of course in some reactions one must take into account the common ion effects, the coagulative action of electrolytes and also increases in precipitates solubility.

In the second case, i.e. 2 above, it is our opinion that a complexing agent which gives a soluble complex with Cu^{2+} maintains a small and practically constant concentration of Cu^{2+} ions during the whole of the titration thereby determining the instability constant of the given soluble complex; this ensures the formation of a copper ferrocyanide of constant composition (in view of the low Cu^{2+} concentration it may be assumed that the activity coefficient is equal to 1; we do not take into account the fact that in aqueous solution it is the aquocomplexes which are present and not the free Cu^{2+} ions).

There is of course no basis for considering that the methods described for getting precipitates of constant composition are confined only to ferrocyanides.

Existing ferrocyanide methods for potentiometric titration of copper [1,2] have not been worked out in sufficient detail; we have therefore tried to find new variants.

EXPERIMENTAL

We used a compensation set-up. A platinum disc ca. 0.4 cm^2 was used as reference electrode. A saturated calomel electrode was used as the auxiliary electrode; the null-instrument was a needle galvanometer ($1^0 = 0.26 \cdot 10^{-8}$A), the electrolytic bridge was a siphon filled with a saturated solution of potassium chloride, the ends being stopped with porous plates.

Preliminary experiments showed that to get a copper ferrocyanide of constant composition the best complexing agent was ammonium hydroxide; this agrees with Kale's results [2]; glycerol and ammonium oxalate are reasonably satisfactory complexing agents.

The results are not reproducible when Rochelle salt is used. On neutralization with sodium hydroxide of the acid formed by substitution of the hydrogen of the hydroxyl groups of this salt with Cu^{2+} ions, no precipitate of copper ferrocyanide is obtained at all. This can probably be explained on the assumption that an inner complex compound of copper is formed in alkaline media and this complex, which is very stable, is not decomposed by the ferro-cyanide.

Ammoniacal, oxalate, and glycerol complexes of copper are sufficiently unstable to be decomposed by ferrocyanide and moreover regulate the copper ion concentration by acting as buffers with respect to the copper.

This property, in our opinion can best be evaluated by calculating the ratio of the copper ion concentration of the given soluble cupri-complex $[Cu^{2+}]_c$ to the copper ion concentration which is determined by the solubility of the precipitate of cupric ferrocyanide formed $[Cu^{2+}]_{ppt}$.

$[Cu^{2+}]_c$ for the oxalate complex was calculated from $\frac{[Cu^{2+}]\,[C_2O_4^{2-}]^2}{[Cu(C_2O_4)_2^{2+}]} =$

$= 6 \cdot 10^{-8}$ [4], the concentration of the $CuSO_4$ solution was = 0.05264 mol/liter;

while $[Cu^{2+}]_{ppt}$ for the cuprammonium complex was calculated from $\frac{[Cu^{2+}]\,[NH_3]^4}{[Cu(NH_3)_4^{2+}]} =$

$= 2.1 \cdot 10^{-13}$ [4], the concentration of the $CuSO_4$ being 0.04753 mol/liter.

In both cases $[Cu^{2+}]_{ppt.}$ was assumed to be equal to $2.5 \cdot 10^5$ g-ion/liter while the concentration of the non-dissociated part of the complex was assumed to be equal to the $CuSO_4$ concentration.

Approximate calculations of the ratio $[Cu^{2+}]_c : [Cu^{2+}]_{ppt.}$ in the case where ammonium hydroxide was used gave a value of 21, while the ratio for the oxalate complex was ca. 17 (we could not find any published data on the instability constant of the copper glycerol complex).

One would expect therefore that the "buffer" action mentioned above will be shown by all soluble complex copper compounds for which the ratio $[Cu^{2+}]_c : [Cu^{2+}]_{ppt.}$ is of the order of 20.

For accurate work, analytical quality reagents were recrystallized from twice-distilled water before use.

$CuSO_4$ solutions were standardized electrolytically. 0.2-0.4 M solutions of $K_4Fe(CN)_6$ were prepared from weighed amounts of $K_4Fe(CN)_6 \cdot 3H_2O$ kept in a desiccator over fused NaBr. The empirical titer of the potassium ferrocyanide with respect to copper was established by the potentiometric method described below.

The molarity of the $K_4Fe(CN)_6$ solution was determined volumetrically by titration with 0.1 N $KMnO_4$ in one case, the latter having been standardized with crystalline sodium oxalate. ca. 0.5 N solutions of Na_2HAsO_3, Na_2HAsO_4 and a 25% solution of ammonia were also among the reagents employed. $Na_2S_2O_3$ was standardized against potassium bichromate.

Copper was titrated in ammoniacal solution as follows: To a known volume of $CuSO_4$ solution continuously stirred with a mechanical stirrer, was added from a buret ammonium hydroxide until the turbidity of $Cu(OH)_2$ just disappeared; this point was checked by observation in the light of an electric lamp. After

addition of a few drops of ca. 0.5 M $K_3Fe(CN)_6$, the solution was titrated with $K_4Fe(CN)_6$; after addition of the aliquots of $K_4Fe(CN)_6$ to the titration flask, the whole was mixed for 2 (or 1) minutes; the stirrer was then switched off and the solution allowed to stand for 2 (or 1) minutes and the compensation point determined.

The maximal value of the potential jump $\Delta E/\Delta V$ was accepted as the respective equivalence point.

The following should be noted: ammonium hydroxide is a suitable complexing agent for another reason, viz. because the cupric ferricyanide is soluble in it while the ferrocyanide is not, even when excess NH_4OH is present; thus, when 0.09290 g of Cu^{2+} in 47 ml was taken and 0.6 ml of 25% ammonium hydroxide added in excess, and the solution titrated with $K_4Fe(CN)_6$ to the equivalence point, no Cu^{2+} could be detected qualitatively in the centrifugate after removal of the copper ferrocyanide precipitate.

We found that the time necessary for stirring the solution during titration and also for letting the solution stand before finding the compensation point may be either 2, or 1 minute each, without sacrificing the accuracy of titration.

By increasing the rate of addition of the working solution the total time for titration can be reduced from 120 to 20 minutes without decreasing the accuracy of the determination; when the time taken is 20 minutes, equilibrium reactions are only established near the equivalence point.

We titrated equal amounts of copper with two $K_4Fe(CN)_6$ solutions of equal molarity (0.2000) prepared at different times from separate aliquots of the salt; and further, using the empirical titrations of these solutions with respect to copper, carried out quantitative determination of copper.

The results obtained are given in Table 1; the errors in both cases are within the limits of experimental error.

TABLE 1

Titration of Cu^{2+} with 0.2 M solutions of $K_4Fe(CN)_6$ prepared at different times

Cu taken, in g	Cu found by titration with $K_4Fe(CN)_6$ T = 0.02569 Cu, in g	Relative error (%)	Cu found by titration with $K_4Fe(CN)_6$ T = 0.02621 Cu, in g	Relative error (%)
0.1162	0.1161	−0.09	0.1172	+0.86
0.1162	0.1165	+0.26	0.1179	+1.16
0.1162	0.1163	+0.09	0.1158	−0.34
0.1162	0.1154	−0.67	0.1160	−0.17
0.1162	0.1155	−0.60	0.1173	+0.95

It is only necessary, therefore, to standardize the $K_4Fe(CN)_6$ once with copper, and then to prepare further $K_4Fe(CN)_6$ solutions of the same concentration by weighing out the same weight of dry salt as used in making up the standardized solutions.

The composition of the precipitate does not correspond to the simple formula $Cu_2Fe(CN)_6$; this was confirmed by the results given below.

On the basis of the amount of potassium ferrocyanide used during potentiometric titration of a known amount of copper, we calculated the ratio of the number of molecules of $CuSO_4$ to $K_4Fe(CN)_6$ corresponding to the composition of the precipitate. We used the molarity of the potassium ferrocyanide calculated

from the weight of salt used. The mean value of the ratio was found to be 2.043. This can probably be explained by the presence of a small amount of basic copper salts in the precipitate.

TABLE 2

Titration of various amounts of Cu^{2+} at various dilutions

$CuSO_4$ solution used, in ml	Molarity of the $CuSO_4$ solution	Cu taken, in g	H_2O added, in ml	$K_4Fe(CN)_6$ used, in ml	$T_{\frac{K_4Fe(CN)_6}{Cu}}$	Cu found, in g	Relative error (%)
9.98	0.07320	0.04645	18	1.777	0.02621	0.04658	+0.28
9.98	0.07320	0.04645	18	1.769	0.02621	0.04636	−0.19
9.98	0.07320	0.04645	30	1.773	0.02621	0.04647	+0.04
9.98	0.07320	0.04645	30	1.761	0.02621	0.04615	−0.65
24.96	0.07320	0.1162	25	4.429	0.02621	0.1161	−0.09
24.96	0.07320	0.1162	25	4.444	0.02621	0.1165	+0.26
24.96	0.1464	0.2324	20	4.473	0.05189	0.2321	−0.13
24.96	0.1464	0.2324	50	4.487	0.05189	0.2329	+0.21
24.96	0.1464	0.2324	87	4.473	0.05189	0.2321	−0.13
24.96	0.1464	0.2324	87	4.467	0.05189	0.2318	−0.26

TABLE 3

Titration of Cu^{2+} in the presence of NH_4NO_3

Cu taken, in g	Volume titrated, in ml	NH_4NO_3 added, in g	$K_4Fe(CN)_6$ used, in ml	$T_{\frac{K_4Fe(CN)_6}{Cu}}$	Cu found, in g	Relative error (%)
0.04645	28.6	0.07	1.776	0.02620	0.04656	+0.24
0.04645	28.6	0.1	1.772	0.02605	0.04616	−0.62
0.04645	29.2	0.3	1.792	0.02605	0.04669	+0.52
0.04645	20.5	0.5	1.858	0.02620	0.04866	+4.76
0.04645	20.4	1.0	2.101	0.02620	0.05501	+18.43
0.1162	52	0.25	4.457	0.02605	0.1161	− 0.09
0.1162	51.3	0.4	4.465	0.02586	0.1155	− 0.60

We also calculated the molar ratios for the results given above with the exception that we used the molarity of $K_4Fe(CN)_6$ determined by volumetric permanganate titration.

In comparison with the ratio of 2.043 adduced above, the molar ratio of $CuSO_4$:$K_4Fe(CN)_6$ corresponding to the precipitate composition increased in these cases to an even greater value of 2.147; we are inclined to ascribe this to the fact that something like less than 3 molecules of water of crystallization enters into the composition of the dry potassium ferrocyanide.

Table 2 contains the results of titrations of various amounts of copper at different dilutions. Within the limits indicated in Table 2, the results can be regarded as satisfactory.

Table 3 contains the results of titrations of copper in the presence of various amounts of an ammonium salt. The results are satisfactory up to the limiting concentrations of NH_4NO_3 used (See Table 3).

We are inclined to explain this by an increase in the solubility of the precipitate under the influence of NH_4 (displacement of the equilibrium toward the formation of NH_4OH at the expense of basic copper salts).

TABLE 4

Titration of Cu^{2+} in the presence of arsenic

Cu taken, in g	Volume titrated, in ml	As added, in g	$K_4Fe(CN)_6$ solution used, in ml	$T_{\frac{K_4Fe(CN)_6}{Cu}}$	Cu found, in g	Relative error (%)
0.04417	19.5	0.10 As^V	1.658	0.02620	0.04342	−1.70
0.04417	19.25	0.10 As^V	1.669	0.02620	0.04371	−1.04
0.04417	47.3	0.10 As^V	1.650	0.02620	0.04321	−2.17
0.04645	43.4	0.025 As^V	1.771	0.02605	0.04613	−0.75
0.04645	30.5	0.03 As^V	1.776	0.02620	0.04656	+0.23
0.04645	31.7	0.03 As^V	1.771	0.02620	0.04613	−0.75
0.04417	93	0.10 As^{III}	1.670	0.02620	0.04373	−0.99
0.04417	75.2	0.10 As^{III}	1.691	0.02620	0.04429	+0.27
0.04417	75.5	0.10 As^{III}	1.702	0.02620	0.04457	+0.90
0.04645	13.7	0.03 As^{III}	1.788	0.02605	0.04658	+0.28
0.04645	12.5	0.19 As^{III}	1.767	0.02605	0.04603	−0.90

Since determination of copper in the pres nce of arsenic – particularly in Paris Green [$3Cu(AsO_2)_2 \cdot Cu(CH_3COO)_2$], is of practical interest, we carried out some initial titrations of copper in the presence of quinquevalent arsenic (Na_2HAsO_4). The results of these determinations are satisfactory, when the ratio of arsenic to copper does not greatly exceed the ratio in Paris Green (see Table 4).

Titration of copper in the presence of trivalent arsenic (Na_2HAsO_3) was unsuccessful, probably because AsO_3^{3-} forms a stable compound with Cu^{2+} in alkaline media [5].

TABLE 5

Potentiometric determination of CuO in Paris Green

Wt. of Paris green, in g	$K_4Fe(CN)_6$ solution used, in ml $T_{\frac{K_4Fe(CN)_6}{CuO}}$ ~~0.03295~~	CuO found, in g	CuO content (%)
0.1667	1.671	0.05507	33.03
0.1667	1.662	0.05476	32.84
0.1667	1.664	0.05484	32.89
		Mean. . .	32.92

We got good results after oxidation of the AsO_3 by the following method. The weakly acid solution containing Cu^{2+} and AsO_3 to which had been added an excess of hydrogen peroxide was heated for 15-20 minutes on a water bath; in order to remove unreacted hydrogen peroxide the test solution was cooled, neutralized with sodium hydroxide using Tropeoline OO as indicator, a 25% solution of ammonia (ca. 1.5 ml) was then added, and the test solution heated again for not more than 3 minutes (this is done in order to avoid separation of copper on the vessel walls as a dense precipitate which is soluble with difficulty in ammonium hydroxide.

After cooling. the test solution was titrated in an ammoniacal medium by the usual method (see Table 4).

Paris green was analyzed by dissolving ca. 5.00 g of it in 0.5 N HCl in a 300 ml standard flask. The solution was filtered and aliquots taken for oxidation of trivalent arsenic and subsequent determination of copper as described above (results are given in Table 5).

The same sample of Paris green was analyzed iodometrically [6]. The results given in Tables 5 and 6 are in good enough agreement for technical analysis.

TABLE 6

Iodometric determination of CuO in Paris Green

Wt. of Paris green, in g	$K_4Fe(CN)_6$ solution used, in ml $T_{\frac{K_4Fe(CN)_6}{CuO}} = 0.007823$	CuO found, in g	CuO content (%)
0.4168	17.60	0.1377	33.05
0.4168	18.00	0.1408	33.79
0.4168	17.80	0.1393	33.43
0.4168	17.50	0.1368	32.83
		Mean	33.27

SUMMARY

1. A method has been developed for the titration of copper in ammoniacal media with a solution of $K_4Fe(CN)_6$ using a ferri-ferrocyanide electrode.

2. Paris green has been analyzed by this method.

3. Attempts have been made to explain the reasons determining the constancy of the composition of copper ferrocyanide.

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A QUANTITATIVE X-RAY SPECTROGRAPHIC METHOD OF ANALYSIS

PART II

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In previous articles [1,2,3], the bases of certain new methods of X-ray spectrographic analysis have been put forward and ways of adapting them to practical use discussed.

In the present communication some of these general observations will be developed further and applied in particular to the analysis of the rare-earth group of elements, which is a classical object for the application of X-ray spectrographic methods. The rare-earths form a group of elements whose chemical properties are very similar. This is the reason for the difficulties which crop up in trying to separate and analyze them. At the same time this is also the reason why they can be fairly easily separated as a group from other elements. The exceptions are yttrium which follows the rare-earths and is usually considered in conjunction with them, scandium, and a few other elements which are sometimes present in small amounts in rare-earth concentrates. In those cases, therefore, where we are concerned with the determination of the content of individual rare-earths in samples where they are present to a considerable extent, the problem may easily be reduced to a quantitative X-ray spectrographic analysis of the individual elements of this group in concentrates containing the sum total of their oxides and a certain amount of other material which can be analyzed separately for yttrium and other elements. Having by some means of other determined either the total content of the rare-earths in the sample or the absolute content of one of them, it is then possible, instead of carrying out a direct quantitative determination of each of the rare-earths, to solve the problem by means of much simpler relative measurements which can be readily carried out with a reliable degree of accuracy. The technique of carrying out these measurements, upon which we have dwelt before [4], has undergone significant changes since that time, and at the present time [3], has been fairly thoroughly worked out. Thus, the analyst's problem can be reduced to the experimental determination of the combination of coefficients n_i in the relations $A_i = n_i A_o$, in which A_i is the content of the i'th rare-earth, while A_o is the content of the element which is taken as the arbitrary internal standard. In the case where the total content S of all the group of elements to be determined in the test sample is known, the final calculation of the sample's composition can be carried out by means of the equation:

$$A_i = \frac{n_i S}{\sum_{i=0}^{i=13} n_i}$$

in which $n_o = 1$.

Let us consider the experimental methods of determining the coefficients n_i which characterize the relative composition of the test mixture. In doing so, let us consider in parallel the two extreme cases – one, in which the test sample contains an appreciable quantity of all the elements comprising the rare-earth group or its fundamental subgroup, and the other where the sample contains only

individual elements of the group considered which can be determined quantitatively[1]). Although each of the methods described [3] is suitable for analyses in both cases, it is expedient to consider in particular under these conditions, those methods which are most convenient for solving the problem on hand. This should, in our opinion favor a more complete clarification, of the advantages and drawbacks of each of the analytical methods considered.

Analysis of Samples which Contain all the Elements to be Determined

In choosing X-ray spectrographic methods of analysis it is natural to prefer those which do not require the construction of a blackening curve.

Among the new methods which have been worked out recently and which belong to the group of "null" methods, which are independent of the shape of the blackening curve, may be included the method which is sometimes called the "spectral line width method" [2]). Its basic principles have already been considered [3]. Here we shall only deal with the most important aspects. The shape of a large class of X-ray lines, to a first approximation, can be described by a dispersion formula, their width and arbitrary cross section can be calculated [8] by the formula:

$$x_n = \Gamma \sqrt{n - 1}\,, \qquad (1)$$

where Γ is the so-called half-width of a line, while n is the ratio of the maximun intensity of the line (I_{max}) to the intensity at any point on the contour of the line (I). The width of the line calculated in this way which corresponds to a definite value of the ratio I_{max}/I, still remains unchanged on the contour of the line which has been deformed on account of the blackening curve, and which is registered on a photographic plate where the ratio between the true intensities of individual points along the contour has been destroyed[3]). Having measured the width of one of the lines to be compared on the spectrogram at the height of maximum blackening of the other line, it is then possible by means of equation (1), independently of the form of function $S = S(I)$, to restore the true ratio of the intensity maximum of both lines, on the assumption that the shape of the emission line is not distorted by registration on a photographic plate. The ratio of the intensities of the two lines being compared when determined in this way is proportional to the ratio of the atomic content of the respective elements in the test mixture (i.e. to the coefficient n_i as used by us above).

Such is the practical method of determining the relative contents of the elements in the test material. However, in order that the method may be used effectively the following conditions must be followed: a) the lines being compared should be near one another; b) the background of each line should be identical. Otherwise when used, this method will come up against a number of difficulties, the necessity of overcoming which will detract considerably from the most important advantage of this method – its simplicity – and will lower its accuracy.

Both these conditions (a and b) are observed in the analysis of rare-earth concentrates containing all the elements. In such a case the fundamental lines of the test group of elements ($L\alpha_{1,2}$, $L\beta_1$ and $L\beta_2$) are located very conveniently[4]) so that, e.g. the $L\beta_1$-lines of element (Z + 2) lie near to the $L\alpha_1$-lines of the Z th element. As a rule they can be used for the successive (one after another) analysis of these elements in a test mixture by the "line width" method.

1) Photometrically.
2) The idea of this method was first put forward in 1937 [5]; its experimental testing and development however, as applied to the problems of optical and X-ray spectrographic analyses have only been carried out comparatively recently [6,7,3].
3) Since the ratio between S_{max}/S and I_{max}/I will be different for different points along the line contour.
4) Unless one takes into account several positions where the lines of the elements are superimposed, and which require great care on the part of the analyst.

In order to do this it is essential in the first instance to know Γ for the respective lines. For this determination a series of standard mixtures of the rare-earths were prepared, the composition of which was selected so that the intensity of the $L\beta_1$ line of one of the elements was equal to 0.5 of the intensity of a nearby $L\alpha_1$ line of another element. After this, the width of the $L\alpha_1$ line was measured at the height of the $L\beta_1$ line of another element contained in the mixture.

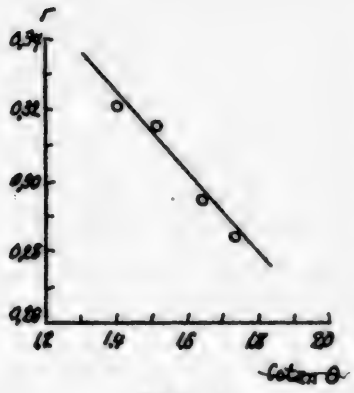

Fig. 1.

The values of Γ obtained in this way for various elements after averaging them on the basis of the results of several measurements were compared with each other. As was to be expected a straight line relation was found to exist between the half-width of the line of an element Γ and the cotangent of the reflection angle (Fig.1). This relation enabled us to calculate the values of Γ for each of the 14 elements of the rare-earth group by relying on the experimentally determined values for those elements which we had at our disposal in a pure state.

A calibration curve was then constructed by means of which it was possible, in our case, to convert from the ratio of the line intensities of the elements compared as determined by the "line

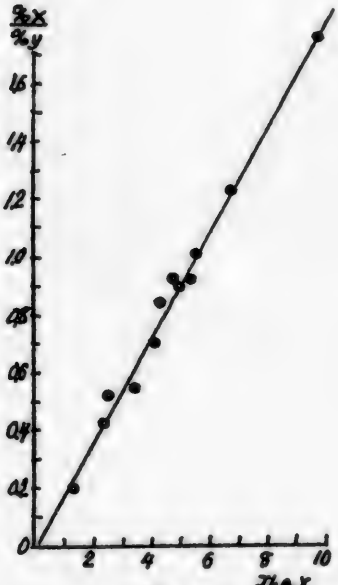

Fig. 2.

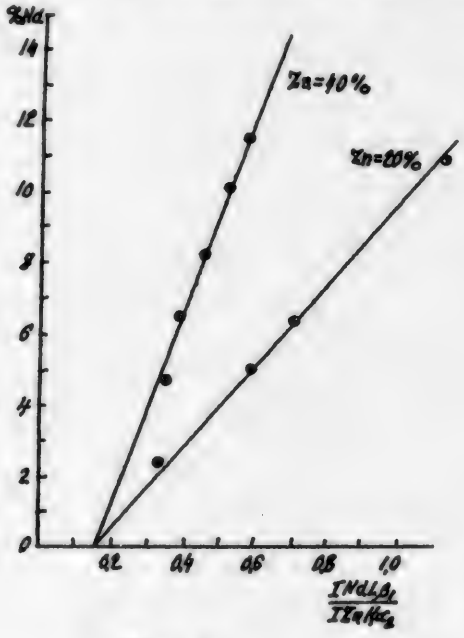

Fig. 3.

width" method to the ratio of their contents in a test mixture. This straight line, which is shown in Fig. 2, was constructed from the results of analyses of many standard mixtures of known composition, and, as was to be expected, remained unchanged for a given pair of compared elements, if the $L\alpha_1$ and $I\beta_1$ lines of each of the elements were chosen so that they lay close to one another. It is worth noting that the straight line in Fig. 2 is in good agreement with theory.

In order to recalculate the relative composition of a test sample on an absolute basis a known amount of a reference standard element was added. In

the case under consideration it is convenient to use zinc[1]) as the reference standard, the amount of the zinc can, generally speaking, be left unchanged in the mixtures, which differ in composition. Nevertheless, for convenience in carrying out analysis we usually introduced ca 20% of the reference standard when the test mixtures contained small amounts of the test elements, while for mixtures with higher percentage contents of the test elements we used 40% of the reference element.

In both cases the absolute content of a test element could be established on the basis of measurements of the width of the Zn $K\alpha_2$-line at the height of the $L\beta_1$-line for neodymium, and by using the straight lines shown in Fig. 3. The accuracy of the method was shown experimentally to be 4-6% of the actual content.

Quantitative X-ray Spectrographic Determination of Individual Elements of the Group

We shall consider next a more general case of analysis. For carrying out this analysis it is necessary to compare the intensities of lines which are located at large and unequal distances from each other against unequal backgrounds on the X-ray spectrograms. Under these conditions the "line width" method is not suitable.

Analysis can, however, be carried out simply and conveniently by a more general method which we have outlined previously [3], and which is based on the application of a transformation of the blackening function.

The latter function P is related to the blackening S by the equation $P = W + \underline{1}(S - W)$, where $S = \log \frac{i_0}{i}$, $W = \log \frac{i_0}{i} - 1$, while $\underline{1}$ is a constant which enables the characteristic curve of the emulsion to be "straightened". It has been shown that this is applicable both in the optical [9], and in the X-ray part of the spectrum [2,3]. In both cases $P = \gamma_p \log I - i_p$ holds for a wide range of line blackening, which practically overlaps all the region the analyst is interested in.

One outstanding feature[2]) of the case under consideration of the use of the P-transformation for carrying out X-ray spectrographic analysis is the independence[3]) of the transformation coefficients $\underline{1}$ and γ_p of the wave-length within the limits of the given part of the spectrum. The P-transformation therefore acquires the character of a universal transformation, the form of which for a chosen type of emulsion and under standard developing conditions is represented quite well by the formula

$$P = W - 1.13\ (S - W). \qquad (2)$$

The actual form of equation (2) is established experimentally by means of the methods described previously [3]. The method given in [1] is used for constructing blackening curves. The relations $P = P(S)$ are given in tabular form. By means of these relations it is possible to convert from blackening values measured with a photometer to P values, and vice-versa. Both the curves used in this work, viz. $S = S(I)$ and $P = P(I)$, are represented on the same scale in Fig. 4.

1) The choice of zinc was a convenient one from our point of view, but its use is not obligatory.
2) In comparison with the general case put forward in [3].
3) As our experiments showed.

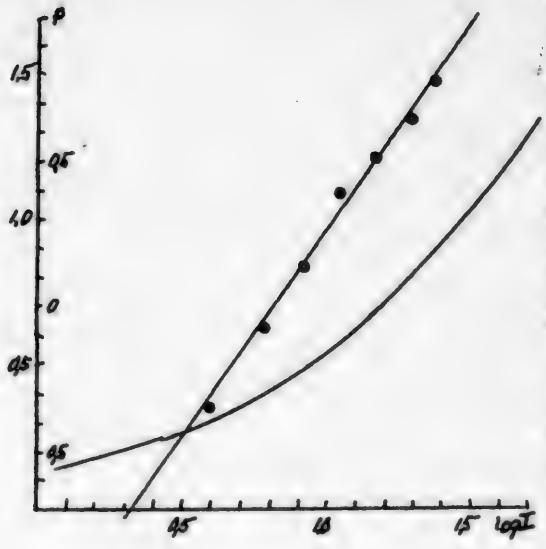

Fig. 4.

A knowledge of $P = P(I)$ enables one to determine the relative amounts of elements in the test mixture easily, independently of whether there are changes in the background values of the X-ray spectrogramm and of the mutual positions of the lines to be compared for the test elements. A series of calibration curves was therefore experimentally determined for this purpose for the elements under consideration, these curves related the values of $\frac{P_1' - P_1''}{\gamma_p}$ determined experimentally to the logarithms of the ratio of the concentrations of the elements compared in the test mixture. The values P_1' and P_1'' characterize the intensity of the lines compared after excluding the influence of the discontinuous background.

Some of these curves, which were obtained on comparing the analogous lines of elements with successively increasing atomic numbers, are shown in Fig. 5.

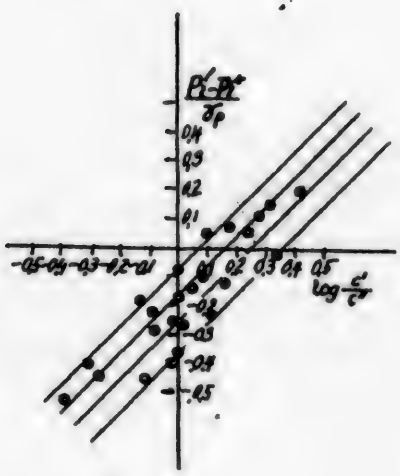

Fig. 5.

The straight line nearest to the origin was obtained by comparing the intensities of the $L\alpha_1$ lines of two elements following straight after each other; the second line by comparison of two elements separated by another element; the third line by comparison of two elements separated by two other elements etc. All of them, as was to be expected in agreement with [3], form a family of parallel straight lines which are separated from each other and make an angle of 45° with the abscissa.

The magnitude of the displacement of one line relative to the next is practically a constant and is equal to ca. 0.09.

Since in the given spectral interval the constant γ_p of the P-transformation, according to our measurements, does not undergo any significant changes, while $i_p' = i_p''$, the experimentally observed variations in the relation $\frac{p' - p''}{\gamma_p} = a + \log \frac{c'}{c''}$, on changing from one straight line to another (Fig. 5) could only be the result of a regular decrease in the sensitivity of the analysis for elements of the group considered in accordance with decreasing atomic number. On the other hand, the nearness of the excitation potentials of the test elements to each other and the complete standardization of excitation conditions of the X-ray spectrum which we try to attain during analysis, are not likely to lead to a similar conclusion; in any case it would be very unreliable. A more detailed treatment of this phenomenon would actually enable one to show that this is not an effect which is specific for the group of elements under consideration, but is a development of certain general geometrical relations which hold for the normal type of models of focussing X-ray spectrographs operating on the principle of internal reflection, and which has strangely escaped the attention of investigators hitherto[1]).

1) As far as we could ascertain from published data.

In actual fact, an indispensable condition for the realization of X-ray elemental analysis by means of a quantitative comparison of the intensities of the X-ray lines of varying wave lengths, is that the strength of the light source remains strictly constant throughout the rotation angle interval used. In X-ray focussing spectrographs with a point source of light the condition is fulfilled automatically, if the source and its image are disposed on a circle touching the curved crystal, the radius of which is twice that of the latter.

For a number of reasons, however, but mainly for the purpose of increasing the overall power of the illumination used (for a given optimal specific loading of the X-ray tube), spectrographs with a focus of finite dimensions are used in practice, the focus being located inside the image circle. It is equivalent to an imaginary point source with high power. It is possible to show that under these conditions, the conditions just mentioned, viz. the uniformity of the power of the light source for every spectral line, is fulfilled only in the case where to a first approximation the value of

$d\omega = \frac{S\theta}{(r - a)^2}$ i.e. the value

$$\frac{S\theta}{\left(\sin\theta - \frac{a}{R}\right)^2} \qquad (3)$$

remains a constant within the limits of the chosen interval of the reflection angle.

Here $d\omega$ is the element of the solid angle; R – the radius of curvature of the crystal; θ – the reflection angle; S – the optimal dimension of the focussing spot for a given reflection agnle and $r = R \sin\theta$.

What has been said above means that in order to create identical conditions for photographing the various lines disposed in a finite interval of the reflection angle, the size of the focussing spot of the X-ray tube of a Johann spectrograph should change according to a trigonometrical law, and should not remain constant as it does in a wide range of the appratus used in practice. Ignoring this fact will lead to the creation of an irregular scale of sensitivity for the apparatus, and to a decrease in the sensitivity with increasing reflection angles. The invariability of the magnitude of the focussing spot of an X-ray tube has as a consequence an actual decrease in the value of the active part of the reflecting crystal for large reflection angles in comparison with small ones.

In this connection, it follows from [3], that the intensities of the spectral lines for values of a/R which are small compared with $\sin\theta$ should decrease as $1/\sin^2\theta$. In the general case where a/R is relatively large, the law of decreasing line intensity with rotation angle is more complicated. Theoretical values of the magnitude of the effect, which can be derived by means of equation (3), appear to be of the same order as the experimentally observed values. Thus relying on a knowledge of the apparatus constants which are at our disposal, it should be possible to forecast the existence of a practically constant value for the displacement of one curve relative to another in Fig. 5 of ca. 0.06 as against the experimentally observed shift of ca. 0.09.

SUMMARY

1. The effectiveness of new X-ray spectrographic quantitative methods has been demonstrated in the case of a group of elements which it is difficult to analyze by other means.

2. It has been shown that for a given active part of the reflecting crystal in a Johann spectrograph in which the source of the X-rays is not located on the image circle and has finite dimensions, there is an optimal size for the focussing spot of the X-ray tube for a given reflection angle. This value to a first

approximation changes proportionally to $1/\sin^2\theta$ and in general depends on the apparatus constants.

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A CARBONATE VARIANT FOR THE MASS SPECTROGRAPHIC ANALYSIS OF OXYGEN IN WATER

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The mass-spectrographic method of determining the isotopic composition of oxygen, which is, generally speaking, the most convenient and rapid method of isotopic analysis, loses its advantages in the direct analysis of water. The difficulties arise in this case as a result of the stability of the vacuum "water" background in the mass spectrometer and particularly as a result of the slowness of evacuation of the residual water vapor when exchanging the water samples being analyzed.

Another obstacle in the analysis of the rare O^{17} isotope is the capacity of water to give – on ionization of its molecules with electrons – secondary ions of the composition H_3O^+.

In order to accelerate the evacuation of water vapor from the ionization tube of the mass spectrometer, and consequently to speed up water analysis, it is possible to lower the adsorption of water by the apparatus walls by carrying out all the analyses in a heated spectrometer tube. An analogous method is used for mass-spectrographic analysis of easily liquefied hydrocarbons, in those cases where the construction of the apparatus enables one to work with a heated tube the method can be applied to the isotopic analysis of water.

It is possible, however, to get over these specific difficulties in the mass-spectrographic analysis of water by another method, viz., by converting the oxygen of the water into another molecular form which is more amenable to analysis. The success of such a method is determined by the simplicity of all the operations necessary for converting the oxygen of the water into the form of an "analytical gas" which can be analyzed readily by the mass spectrometer.

The best gas for isotopic oxygen analysis is CO_2 because of its ease of separation and purification, its ease of evacuation from a vacuum system, the purity of the vacuum background of the mass spectrometer in the region of the isotopic peak of CO_2 (masses 44-46), and finally because of the high ionizability of its molecules by electrons. In addition, the capacity of CO_2 to exchange oxygen with water enables one to introduce the oxygen from the test water into the CO_2.

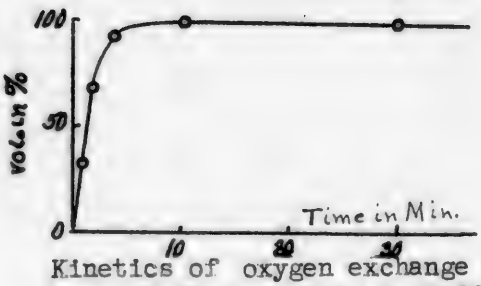
Thus, isotopic analysis of water can be replaced by a much more convenient analysis of the oxygen of carbon dioxide, if one can guarantee beforehand complete exchange of oxygen between the water tested and the small amounts of CO_2 taken in definite amounts.

An analogous method for oxygen exchange in the system CO_2-H_2O has been used for the precision mass-spectrographic determination of heavy oxygen O^{18} in samples of sea water [1]. It is also obvious that this principle of the exchange and transfer of the oxygen under test into the "analytical" gas CO_2 is applicable for studying the composition of oxygen in other oxygen-containing compounds which are difficult to analyze, e.g., silicates, alumino-silicates, and oxides, if it is possible to find and work out the conditions necessary for realizing complete

oxygen exchange between these compounds and CO_2.

Below we discuss the basis of a very convenient and simple carbonate variant for the isotopic analysis of water oxygen which does not require any additional apparatus; this is followed by a description of the actual technique employed.

This variant is based on the following results on the oxygen exchange between alkali carbonates and water.



Kinetics of oxygen exchange between K_2CO_3 and H_2O at 100°C.

According to experiments carried out by Mills and Urey [2], at room temperature, free CO_2 exchanges its oxygen for the oxygen of water at a moderate velocity, the time of half exchange $\tau = \approx 20$ minutes. Oxygen exchange between bicarbonates and water is somewhat slower, while the rate of exchange between normal carbonates and water is extremely low, the half exchange time $\tau = \approx 2$. days.

Increasing the temperature, however, has a considerable effect on the kinetics of oxygen exchange of dissolved carbonates; at 100° the oxygen of the water exchanges not only with bicarbonates CO_2 but with normal carbonates so rapidly that the respective constants can only be evaluated approximately; the half exchange time of K_2CO_3 with water $\tau = \approx 1$ minute, while exchange is practically complete after 10 minutes

The graph shown in the Fig. illustrates the curve we obtained for the kinetics of oxygen exchange between K_2CO_3 and water, during a study of the interaction of H_2O enriched with the O^{18} isotope with normal K_2CO_3. Similar experiments with sodium carbonate and CO_2 gave identical results; the exchange was so rapid that it was impossible to distinguish between carbonate and bicarbonate.

These experiments were carried out as follows. The carbonate solution was prepared first. 0.5 g of K_2CO_3 (normal composition) was dissolved in 10 ml of water enriched with O^{18} (1%). A test tube containing the solution was then immersed in a steam bath; after varying time intervals of 0, 1, 3, 10, 30 minutes, 1 ml aliquots were removed and rapidly (8 minutes) evaporated on a watch glass. The dry residue of carbonate was transferred on a boat to the inlet system of a mass-spectrometer, where the CO_2 was liberated from the carbonate into a vacuum by addition of pyrophosphoric acid. The extent of exchange was determined by the ratio of the isotopic peaks of CO_2 of masses 45 and 46, respectively.

The rapid assimilation of water oxygen by the dissolved carbonate at 100° enables one to evolve a very suitable form of the carbonate method of analyzing the isotopic oxygen composition of water. The following procedure can be recommended.

Into a small, dry test tube 50 mg of dry potassium carbonate is weighed out and 1 ml (or 0.5 ml) of the test water added to it. The test tube containing the dissolved potassium carbonate is stoppered and kept in a boiling water bath for 20 minutes so as to ensure complete exchange. The contents of the test tube are then poured out (no rinsing) on to a watch glass and rapidly evaporated to dryness on a sand bath. The dry carbonate containing the "water oxygen" is then analyzed in the mass spectrometer.

For comparative testing, exactly the same procedure must be adopted for the

water taken as the standard, so that all the results can be related to the same standard. Comparative analyses increase the accuracy and simplify the calculation of results (see below). During analysis of a series, the exchange procedure should be carried out in one apparatus. The dry carbonate obtained after exchange can be kept in a desiccator (in order to avoid a reverse exchange) over solid NaOH.

The composition of the oxygen in the CO_2 evolved from the carbonate after exchange is not exactly the same as that of the oxygen in the test water. The ratio of O^{18}/O^{16} of this CO_2 and of the carbonate will differ from the O^{18}/O^{16} ratio of the water by a correction factor which depends on 1) the relative amounts of oxygen in the water and in the carbonate; and 2) on the constant of the isotope equilibrium in the system CO_3^{2-} - H_2O for oxygen at 100°. A knowledge of this correction, and consequently of the O^{18}/C^{16} of the original water can be calculated from the analytical results.

Let:

q and q' represent the percentage ratio O^{18}/O^{16} of the test water before and after exchange with K_2CO_3 respectively;

q_k and q_k represent the percentage ratio of O^{18}/O^{16} in K_2CO_3 before and after exchange.

m,n the relative number of oxygen atoms participating in this exchange in the carbonate and water respectively. It is then easy to show that

$$(q'_k - q_k) \cdot m = (q - q') \cdot n. \qquad (1)$$

The ratio of q' to q'_k is the constant of the isotopic equilibrium in the system H_2O - CO_3^{2-} at 100°. This ratio was calculated by Urey [3] and found to be equal to

$$K = q'/q'_k = 0.99 \qquad (2)$$

The ratio O^{18}/O^{16} of normal carbonate is ca. 0.2%; consequently $q_k = 0.2$. The value of O^{18}/O^{16} for water can then be calculated from the expression:

$$q = q'_k \cdot \left(0.99 + \frac{m}{n}\right) - 0.2 \cdot \frac{m}{n}. \qquad (2)$$

The value of q'_k for this equation was determined on the mass spectrometer as half of the percentage ratio of the 46 and 44 peaks of CO_2 evolved from the "exchanged" carbonate.

If the potassium carbonate and water used for the exchange are mixed in the ratio 5:100 or 10:100, then the value of m/n will be 0.02 or 0.04 respectively. Other ratios of m/n of course are permissible, within the limits of potassium carbonate solubility.

In comparative analyses one usually determines by how much the O^{18}/O^{16} of the test water exceeds that of a standard, i.e.

$$\Delta q = q - q_{stand}$$

is found.

From equation (2) it follows that this Δq of water is related to the respective increase $\Delta q'_k$ of the exchanged carbonates as follows:

$$\Delta q = \Delta q'_k \left(0.99 + \frac{m}{n}\right). \qquad (3)$$

For a 5% ratio of K_2CO_3 and H_2O, equation (3) has the form

$$\Delta q = \Delta q'_k \cdot 1.01$$

The method described is applicable to the analysis of oxygen in water enriched with heavy isotopes to give results with the usual accuracy of mass spectrographic methods. The applicability of the carbonate method for precision analysis of O^{18}/O^{16} of natural waters has not been studied.

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THE INDUSTRIAL IMPORTANCE OF ASCORBINOMETRY

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Commercial synthetic ascorbic acid is available in preparations of exceptional purity and can therefore be used for standardizing alkali solutions. In the case of ascorbic acid, however, its acidic properties are of secondary importance compared to its reducing properties, which are unusual for organic compounds and are the bases of its biological activity. Its reducing properties are the basis of methods used for determining "Vitamin C", since in the form of pure preparations it is easily titrated with iodine and can also be determined by the blue dye dichlorophenolindophenol, which reacts stoichiometrically with it. Analytical work relating to ascorbic acid has hitherto been confined to its determination, and only a few papers have been devoted to the use of its reducing properties for the determination of other materials. Without taking into account the preparation of certain colloids, and the determination of the noble metals with ascorbic acid, shortly before us, the Russian research workers Ptitsyn and Kozlov [1], used ascorbic acid for the potentiometric determination of trivalent iron. Fearing rapid decomposition of ascorbic acid in solution, they prepared fresh solutions every time, and during titration they added a known excess of ascorbic acid in the solid state and titrated the excess with 0.1 N iodine.

The authors [1] did not propose a method for working solutions of ascorbic acid which retain their reducing properties over long periods, nor considered the possibility of using ascorbic acid in other oxidation-reduction reactions. Because of its strong reducing properties, solutions of ascorbic acid are oxidized fairly rapidly, but the process only occurs rapidly, according to our work, in the presence of traces of metals which catalyze its oxidation. If, therefore, water which has been distilled in an all-glass apparatus free from any metals, particularly copper, is used for making the working solution, then its strength depreciates only to a very small extent even in air; when kept under CO_2 it retains its strength for weeks. On the basis of our work we can ascribe the decomposition of working solutions of ascorbic acid to two causes. Freshly prepared solutions initially lose their strength because of aerial oxidation catalyzed by copper ions. This decomposition amounts on an average to 0.3% per day when a solution which has been prepared from water distilled once in a glass apparatus is exposed to air. Subsequently, after a fairly long time, bacterial decomposition sets in, so that decomposition of a solution kept in an inert atmosphere sets in usually after 1-2 weeks. It became obvious that to prevent aerial oxidation it is necessary to complex copper ions or to convert them into insoluble precipitates. The suggested use of cyanides, thiocyanates and sulfides of the alkali metals is not a good one, because the presence of these salts severely limits the application of ascorbic acid solutions, and in any case these salts are not very effective. The proposal made very recently [2] that Trilon B (Complexone III) be used for the

protection of ascorbic acid solutions does enable the catalytic activity of copper ions to be eliminated completely and thus increases the storage time of the solutions. Trilon B also hinders bacterial decomposition so that the solution can be stored for several months. It is best to keep solutions in a refrigerator at ca. +2°. A solution preserved by addition of Trilon B and stored in a refrigerator may be regarded as reasonably stable for a period of some months; we found that such a solution kept better than thiosulfate solutions.

Ascorbic acid solutions may be standardized by titration against 0.1 N iodine or against the iodine liberated on interacting postssium iodide with potassium iodate or biiodate. The results obtained are very accurate. Addition of starch at the end point is not recommended, since the starch slows down the reaction considerably. Standard ferric chloride can also be used for checking the standardization of ascorbic acid solutions.

It is advisable to prepare 0.01 N solutions of ascorbic acid freshly from 0.1 N solutions, although one keeps just as well as the other according to our work.

Bearing in mind the cheapness of ascorbic acid, it is reasonable to expect that it will take its place among other reducing agents.

The use of ascorbic acid solutions for the determination of a few oxidizable solutions was studied, and in some cases satisfactory results were obtained. Durint these preliminary tests the end point was chiefly determined potentiometrically. We have suggested the term "Ascorbinometry" for these methods [3]. We also established that ascorbic acid can be used in the molybdenum blue reaction for the determination of phosphates, arsenates, silicates and germanates. The oxidation of ascorbic acid depends on the nature of the oxidizing agent used.

Ascorbic acid is oxidized by oxidizing agents of average strength to dehydroascorbic acid; this process is fairly well defined and proceeds reasonably fast, so that for the majority of cases the fundamental reaction may be written:

$$C_6H_8O_6 = C_6H_6O_6 + 2H^+ + 2e.$$

It is often expedient to accelerate this reaction by means of catalysts or by heating the reaction mixture. Sometimes, particularly in hot solutions, the oxidation goes further until oxalic acid and l-threonic acid are formed. Strong oxidizing agents convert the latter into oxalic acid. If one bears in mind that hydrogen ions are formed during oxidation it is clear that the conditions for carrying out the individual methods must be carefully observed. During such investigations it is essential to establish the well defined course of the reaction, and to find the necessary conditions for carrying it out.

Determination of Trivalent Iron

From a practical point of view the determination of iron is of great interest, so that using the results of the Russian research workers mentioned already [1], we accordingly tried to develop a method for its determination. First of all it was necessary to elucidate the mechanism of the reaction and then to select the appropriate conditions for carrying it out. It was established that the reduction of trivalent iron ions, particularly in dilute solutions, proceeds slowly, and that the presence of thiocyanates slows down the reaction still more. In neutral solutions which are too hot, even dehydroascorbic acid can act as a reducing agent, as a result of which low results are obtained. Taking all these factors into consideration, titration should be carried out exactly as described below.

An almost neutral or neutralized solution of the trivalent iron salt is acidified with 5 ml of 2 N hydrochloric acid and titrated with 0.1 N ascorbic acid

solution to the point where the yellow color of the solution disappears. The contents of the beaker are then heated to 60° and to the hot solution is added 1 ml of 0.5 N potassium or ammonium thiocyanate and the titration continued until the red color of the solution is not decolorized after standing for a few seconds. It is expedient to finish the titration within 5 minutes of starting to heat the solution and to try and get a final volume of ca. 100 ml. The accuracy of the method is 0.1%.

The determination, which is rapid and can be carried out without any special apparatus, gives very accurate results (see Table 1). The special advantage of the method is that it is applicable in the presence of nitrates, and in the presence of phosphates and fluorides; in this connection, it is the only method. Strong oxidizing agents such as nitrites naturally interfere, but their removal or the suppression of their influence is not usually difficult. The procedure described above can also be used for 0.01 N solutions.

TABLE 1

	mg Fe/ml			
In the form of Fe_2O_3 gravimetrically	Volumetric method			
	Ascorbic acid	Titanometrically	Zimmerman-Reinhart	Iodometrically
5.933	5.969	5.964	5.964	6.005
5.975	5.958	5.958	5.952	5.994
5.978	5.964	5.964	5.975	5.977
5.954	5.969	5.969	5.986	5.972
Mean 5.960	5.965	5.964	5.969	5.992
	Deviation of individual methods, in %			
-0.16	-0.08	-0.10	-0.02	+0.37

These advantages make the method a suitable one for industrial application. Recently the unusual increase in the practical application, particularly in production laboratories, of titanometric, chromometric, and vanadometric methods of determining trivalent iron has shown that these methods fulfill their purpose very well. It is the rapidity of reductometric methods for iron which is their chief advantage.

The conditions which necessitate keeping the working solutions under a protective gas and also titrating in an atmosphere of this gas, since basic reactions induce aerial oxidation, is a drawback of these methods as compared with oxidometric methods. It must be admitted, however, that the reductometric methods enumerated above have ousted oxidometric methods in modern laboratories because of the simplicity of preparation of test solutions, which in the majority of cases already contain the iron in a trivalent form. After removal of the nitric acid usually used for oxidation, the solution of trivalent iron can be titrated directly in the presence of a suitable indicator. When the ascorbinometric method is used there is no need to keep the solution under a protective gas and it is sufficient to check the standardization of the ascorbic acid solution once a day. Nitric acid does not interfere in the ascorbinometric determination of iron; the solution obtained, therefore, after dissolving the iron, can be titrated without evaporation of excess nitric acid. Titration in this manner is not sensitive to atmospheric

oxygen so that there is no need to use a proctective gas. Ascorbinometric determinations of iron in comparison with other reductometric methods used in practice is less sensitive to interfering ions for an equal rate.

From what has been said above one may expect that the ascorbinometric determination of iron will be rapidly adopted in production laboratories and will take its place among more complicated reductometric methods. The fact that nitrates, phosphates, and fluorides in small amounts do not interfere with ascorbinometric determinations should contribute to making it a popular method. From this it follows that oxide, sulfide, and carbonate iron ores can be titrated directly after dissolving them in a mixture of nitric and sulfuric acids, while iron solutions after passing through the most diverse processes of separation can still be used for determination of the iron content after oxidation with nitric acid or hydrogen peroxide. These advantages are made most clearly evident in the determination of the iron content of bauxite, and in the usual analyses carried out in glass and ceramic laboratories. The method is eminently suitable for determination of iron in "luminous powders", the iron in these powders being present as the prosphates and fluorides. The iron can be determined directly by dissolving the sample in acid, oxidizing the iron with hydrogen peroxide and destroying the excess peroxide before titrating.

Titration can be accurately carried out by depolarization methods. A voltage of 0.14 V is applied to two platinum electrodes immersed in the solution to be titrated through a shunted micro-ammeter. When such a scheme is employed there is no need to use an indicator and the titration can be carried out in colored and completely opaque solutions. It is convenient to use this variant, particularly in the presence of large amounts of Cr^{3+}, Ni^{2+} or Co^{2+}. The method is definitely a superior one for the determination of iron in metallic nickel, ferrochrome, and in chrome steels. A thermocouple placed in a gas burner flame can be used for measurements, no other special apparatus is required, so that this method cannot be ignored from the production laboratory point of view. The equivalence point can also be determined polarometrically(amperometrically) in this method.

Determination of Chlorates [5]

Ascorbic acid solutions are suitable for titrating iodine liberated from potassium iodide by oxidizing agents in acid media, and can practically completely replace sodium thiosulfate. This is true also in the case of chlorate ions; in this case however we have managed to find a direct titration method. The obvious advantage of this method is that it is a direct one. After a consideration of the general methods known for the determination of chlorates we came to the conclusion that chlorate ions, which are particularly stable because of the symmetry of their electronic system, are reduced only in strong acid media, and only in auto-catalytic or catalytic processes. We therefore had first of all to establish whether ascorbic acid can be used in strong acid solution, and then find a suitable catalyst. It was established that under conditions where the reduction of chlorates is speeded up, the ascorbic acid which is in excess during titration does not decompose appreciably, even in 4N sulfuric acid at 60°. The catalysts which are normally used in oxidation-reduction titration processes proved to be useless for our purpose. Selenious acid, however, proved a suitable indicator; at the end point in this case, elemental selenium is released. In a series of careful experiments it was established that excess chlorates are not reduced under the optimal conditions for determination of dehydroascorbic acid. During a study of the effect of other ions it was found that reproducibility of results was better in the presence of Mn^{2+} ions, since in this case a local excess of ascorbic acid does not lead to a premature separation of selenium. Taking into account all these factors, the following technique may be adopted.

To the solutions containing chlorate are added 8 N sulfuric acid and distilled water in such amounts that at the end of titration the sulfuric acid concentration is 4 N while the final volume is 100 ml. The solution is then heated to 60° and 10 ml of 0.1 M selenious acid added together with 5 ml of 20% $MnSO_4$ solution. 0.1 N ascorbic acid is added from a buret with vigorous stirring until 1 ml has been added, when the solution is again heated to 60° and titration is continued till a definite orange color appears. At this point one should wait not less than 10 seconds after the addition of each drop.

TABLE 2

Test material	Active chlorine content, %	0.1 N ascorbic acid used (ml)	Found	
			$NaClO_3$ (g/liter)	$Ca(ClO_3)$ (g/kg)
100 ml freshly prepared solution of NaOCl.....	0.79	0.15	0.0027	
100 ml freshly prepared solution of NaOCl + 5 ml 0.1 N $NaClO_3$ solution.....	0.79	5.17	0.0917	
100 ml freshly prepared solution of NaOCl + 10 ml 0.1 N $NaClO_3$ solution.....	0.79	10.20	0.1809	
100 ml freshly prepared solution of NaOCl + 20 ml 0.1 N $NaClO_3$ solution.....	0.79	20.12	0.3569	
100 ml solution of NaOCl after standing 14 days....	5.92	2.86	0.0507	
10 ml of commercial hypochlorite solution.....	3.63	33.50	5.943	
5 ml of NaOCl solution after standing for a few months.....	5.38	45.55	16.163	
1.00 g of chloride of lime	27.80	17.80		36.64

This method does away with the use of expensive iodine compounds, but is not inferior to other methods of determining chlorate with respect to accuracy. This method can be applied to the determination of chlorates in hypochlorites. It was found that on boiling with H_2O_2 in alkali solutions, hypochlorites are broken down without formation of chlorate, while the chlorate can be determined in the acidified solution by the method described above; the results are given in Table 2. This method is applicable to the determination of chlorates in bleaching powder and in the alkali metal hypochlorites, and also in the mother liquors resulting from the electrolysis of alkali metal chlorides.

Determination of Iodates

We have also found a direct method for determining iodates [6], without using potassium iodide. It was established that on titrating solutions of potassium iodate in acid media without addition of potassium iodide the iodide ions formed on reduction react with excess iodate ions to give iodine, which temporarily settles out in the solid form and which only reacts with ascorbic acid after complete reduction of the iodates; the end point is determined by the complete disappearance of elemental iodine. We succeeded in increasing the accuracy of the method further on the basis of the fact that the iodide ions formed as intermediates can by complexed with $HgCl_2$. As a result, the reduction of iodate can proceed in one stage without a transitional separation of iodine. Determination

of the end point is based on the fact that excess ascorbic acid reduces mercuric chloride to mercurous chloride. Mercurous chloride, however, only precipitates at the end of the titration when selenious acid is used as a catalyst. Determinations were made as follows:

The neutral or neutralized solution of iodate is acidified with 10 ml 0.1 N HCl, and then 10 ml of 0.1 N selenious acid and 15 ml of a saturated solution of mercuric chloride added, water being then added until the final volume is ca. 100 ml. The solution thus prepared is titrated with 0.1 N ascorbic acid, titration being slowed down toward the end point, and the slightest turbidity is taken as the end point.

The method was proved to be very accurate even when using 0.01 N solutions, although a small indicator error creeps in thereby. The method is capable of wide application, because by its application iodides and even free iodine can be determined, if the solution is first treated with bromine water and the iodides converted into iodates, the excess bromine being removed with formaldehyde. This "multiplication" method among other things enables one to repeat a determination, the iodide present in the already titrated solution being again oxidized to iodate (see Table 3).

Table 3

0.1 N KI (ml)	0.1 N ascorbic acid solution used in ml		
	First	Second	Third
20.00	19.97	19.95	20.08
	19.97	20.06	20 06
	19 99	19.82	20.10
	19.98	20.06	20.04

Table 4

Sample No. 1		Sample No. 2	
mg I_2/ml	mg KI/ml	mg I_2/ml	mg KI/ml
66.0	20.9	66.0	24.8
66.0	21.0	66.1	25.0
66.2	20.6	66.1	25.2
66.2	21.0	66.2	25.0

Bromine dissolves the calomel, while it converts the dehydroascorbic acid into an oxidation product which does not interfere. This cheap method is suitable for the determination of iodine content in iodine compounds and also in mineral waters. The advantages of this method are clearly demonstrated in the analysis of tinctures of iodine (see Table 4), in this case one can first of all determine free iodine after dilution with alcohol and then after removal of alcohol and oxidation with bromine the total iodine content can be determined, all with one working solution – ascorbic acid. Moreover, this method is accurate and more rapid than the methods of determination used in pharmaceutical chemistry.

Determination of Bromates

The determination of bromates [7], with ascorbic acid is carried out in a similar way to that for iodates. This method is only of importance for the analysis of alkali metal bromates.

Ascorbinometric Determination of Quinquevalent Vanadium

We have hitherto developed two methods; one a rapid method which is reasonably accurate for production analysis, and the other a more accurate one which has, however, a more restricted use. The first method is based on direct titration of quinquevalent vanadium in acid media with ascorbic acid to give quadrivalent vanadium. For the detection of the end point two new oxidation-reduction indicators - p-methoxy and p-ethoxy diphenylamine are used. Quinquevalent vanadium oxidizes both indicators to a dark violet color, while ascorbic acid in reducing them also decolorizes them. The color change is reversible, but over a prolonged time quinquevalent vanadium itself uses up the indicator, i.e. an irreversible oxidation

takes place to an insignificant extent. This fact, however, does not affect the practical application of the indicators. The accuracy of titration is of the order of a few percent; this is a result of the fact that dehydroascorbic acid reduces quinquevalent vanadium, though slowly, while the interaction between ascorbic acid and quinquevalent vanadium is also slow. When, however, the titration is carried out rapidly, and this can be done easily after practice, the deviation of the results becomes very small. This method is recommended particularly for rapid technical analyses, e.g. for the determination of vanadium in vanadium or clay factories. An aliquot of the vanadium solution is dissolved in a small volume of sulfuric acid and the vanadium oxidized to the quinquevalent stage with potassium permanganate, excess of which is destroyed with oxalic acid; the quinquevalent vanadium is then titrated with 0.1 N ascorbic acid in the presence of p-ethoxy or p-methoxy diphenylamine. The determination can be repeated if the quadrivalent vanadium is first oxidized back again to the quinquevalent stage.

The more accurate method consists in adding excess ferrous sulfate to the acidified test solution of quinquevalent vanadium, through a reduction tube filled with metallic cadmium, whereby an equivalent amount of trivalent iron is formed, which is equivalent to the quinquevalent vanadium present; this trivalent iron is then titrated with 0.1 N ascorbic acid, using thiocyanate as indicator. Consequently instead of the highly oxidized quinquevalent vanadium, a system with a considerably lower oxidation-reduction potential is titrated; as a result the determination is more accurate because the dehydroascorbic acid does not react under these conditions.

Ascorbinometric Determination of Quadrivalent Cerium in the presence of ferroin as indicator has been carried out. The use of ascorbic acid is being extended for the determination of other oxidizing agents, and we hope that it will find even wider application.

Among further possible applications of ascorbic acid we may mention the determination of oxygen dissolved in water and the oxygen content of various gas mixtures. The importance and industrial significance of these determinations are obvious. In this connection a reduction pipet which we have designed may be useful. A solution of ferrous sulfate which does not contain any trivalent iron is added to the test water through the reduction pipet filled with powdered metallic cadmium, so as to form a separate layer underneath the water; the solution of ferrous salt is then vigorously shaken in a hermetically sealed flask, whereby the $Fe(OH)_2$ reacts to form $Fe(OH)_3$ in an amount equivalent to that of the dissolved oxygen. The hydroxide is allowed to settle and hydrochloric acid is carefully added to dissolve the precipitate; the solution of ferric chloride is then titrated with ascorbic acid. When only a small amount of dissolved oxygen is involved, the trivalent iron is determined colorimetrically with ammonium thiocyanate. Our results indicate that the method is fully equivalent to Winkler's method. Even the Winkler method can be converted into an ascorbinometric method if a strongly acidified solution of ferrous sulfate is added to the precipitated manganous hydroxide through the reduction pipet, and the trivalent iron titrated with ascorbic acid. Oxygen may be determined in gas mixtures on the basis of this method. Ferrous sulfate and sodium hydroxide are added in succession to a gas buret of known volume; after oxidation and acidification the trivalent iron ions, which are formed in an amount equal to the oxygen content are titrated. This method is of considerable importance for the determination of oxygen in boiler water and tap water and also in gas analysis. One of our future problems is the micro-determination of oxygen, in which the oxygen reacts directly with ascorbic acid in the presence of a catalyst.

Other Applications of Ascorbic Acid

Among other possible analytical applications of ascorbic acid we may

mention micro-colorimetric determination of phosphates, germanates [8], silicates, and arsenates. Methods have already been worked out in full for the first two. The method is suitable for the quantitative determination of traces of phosphates. Mention may be made of the determination of phosphine in acetylene, in which only a very small amount of gas is necessary for analysis. The method for germanate is of interest from the point of view of ore prospecting. It is pertinent to mention here the recent successes of Soviet research workers on ultra-violet titration [9], in which ascorbic acid can be titrated with a solution of ferric chloride, the end point being determined by the capacity of the ferric chloride solution to absorb the ultra-violet, while the ascorbic acid does not.

What has been said above clearly shows that a number of analytical problems which are of industrial importance have already been solved. One can assume that further research into the possibilities of the method will facilitate the analyst's work, and make it simpler and more reliable.

One must mention that nearly all my colleagues at the Department of General Chemistry of the Budapest Polytechnical Institute participated in the development of "Ascorbinometry", in particular I refer to Dr. E. Bodor and B. I.Papp, who did most of the work.

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A SPECIFIC METHOD FOR THE DETERMINATION OF CARBONYL GROUPS IN HYDROXYCELLULOSES

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We have shown previously [1], that apart from carboxyl and aldehyde groups there are also keto groups in certain hydroxycelluloses. In order to determine total carbonyl groups in hydroxycellulose a method has been suggested which is based on condensation with hydroxylamine hydrochloride [2]; the method was first used for the quantitative determination of carbonyl groups by Petrenko-Kritchenko in 1901 [3].

The method is based on the following reactions:

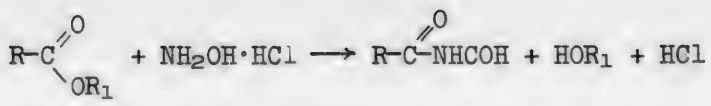
$$R - C(=O)H + NH_2OH \cdot HCl \rightarrow R - C(=NOH)H + H_2O + HCl$$

$$R - C(=O) - R_1 + NH_2OH \cdot HCl \rightarrow R - C(=NOH) - R_1 + H_2O + HCl$$

Oxime formation occurs in weak acid media at a pH of 5-6. The carbonyl groups are estimated from the amount of hydrochloric acid released. There are certain characteristic features of this reaction when applied to carbohydrates. It has been established that certain sugars react rapidly with hydroxylamine – 1-1.5 hours (maltose, galactose, arabinose), while others react slowly – 10-18 hours, (glucose, fructose, cellobiose). The percentage of carbonyl groups found experimentally in the sugars is 95-103% of theory. When working with hydroxycellulose the reactions occur in a heterogenous medium. It has been found that with hydroxycelluloses obtained by oxidation with CrO_3 and HIO_4 the reaction proceeds relatively quickly – 1.5-2 hours. The presence of carboxyl groups interferes with the determination, since under the experimental conditions (pH 5-6) the carboxyl groups can also react with hydroxylamine to form salts. Carboxyl groups should, accordingly be neutralized first of all by treating the test material with a calcium acetate solution. The accuracy of the method has only been checked on hydroxycelluloses prepared by periodate oxidation, and containing large amounts of aldehyde groups and small amounts of carboxyl groups; it was found that the reproducibility is of the order of $\pm 1\%$.

We tried the method for the determination of keto groups in hydroxycelluloses. In addition to determining total carbonyl groups by the hydroxylamine method, we also determined aldehyde groups iodometrically [4]. The amount of keto groups was determined by difference between total carbonyl and aldehyde groups.

Having tried the hydroxylamine method, we soon found that it possesses a number of drawbacks, the main one being its lack of specificity. We have previously established that in hydroxycelluloses obtained by oxidation with hypochlorites in acid media, or those subjected to prolonged de-ashing with acids, lactone bonds are formed as a result of interaction between neighboring carboxyl and hydroxyl groups. Lactone groups, just like complex ester groups, can react with hydroxylamine to form hydroxamic acids.



This reaction, according to published data, can occur in weakly alkali, neutral, or weakly acid media. We have demonstrated the formation of hydroxamic acids by condensation of hydroxycelluloses, prepared by hypochlorite oxidation with $NH_2OH \cdot HCl$, by qualitative tests for hydroxamic acids [5]. After interaction with hydroxylamine in a weakly alkali medium, the hydroxycellulose acquires a rose color on testing with $FeCl_3$ in a weakly acid solution as the result of complex formation between iron and the hydroxamic acids. As a result of this secondary reaction, results of titrations of HCl liberated are higher than the true content of carbonyl groups in the hydroxycelluloses. In order to avoid this it is essential, therefore, to increase the specificity of the method, and this was achieved by lowering the pH during condensation from 5-6 to 3-4. In a more acid medium only the carbonyl groups react; the lactone groups do not condense. Since at such a low pH a partial hydrolysis of the oxime is possible, the aqueous medium was replaced by an alcoholic one. The completeness of condensation of the carbonyl groups at a pH of 3-4 was checked by comparing the results of determination of aldehyde groups in hydroxycellulose by two methods, first, by condensation with hydroxylamine in alcoholic media at a pH of 3-4, and second, iodometrically. The results obtained by both methods were in good agreement; e.g. the following results were obtained:

1) by the modified hydroxylamine method - 0.109% CHO groups

2) iodometrically - 0.115% CHO groups.

This confirms that the cellulose carbonyl groups react quantitatively with hydroxylamine at a pH of 3-4.

In order to obtain a more convincing proof of the participation of lactone groups in the reaction with hydroxylamine during the determination of carbonyl groups, the following test was made. Hydroxycellulose was worked up with a 1% solution of sodium carbonate at 40° for 30 minutes in order to destroy the lactone bonds. After washing with water and drying in air, determinations of the carbonyl groups in an aqueous medium at pH 5-6 and also by the new method in an alcoholic medium at pH 3-4 gave similar results. Use of the method involving an aqueous medium at pH 5-6 gave a value of 0.18% keto groups, while the new method in which an alcoholic medium at pH 3-4 is used gave a value of 0.17%. Both methods, therefore, gave the same results in the absence of lactone groups. In practice, however, we cannot recommend a method in which the lactone groups are destroyed beforehand by an alkali treatment, because, as is known from previous work, even a short time in the alkali medium can lead to partial solution of and change in the hydroxycellulose.

Another drawback of the hydroxylamine method of determining carbonyl groups in hydroxycellulose is the impossibility of standardizing the results obtained by titration of liberated HCl, against determinations of the nitrogen combined during condensation.

Using the hydroxylamine method, we calculated the total aldehyde + keto groups from the titration results. The values obtained were checked against the nitrogen content of the oximes formed. In order to do this the hydroxycellulose which has reacted to give the oxime was carefully washed with water and dried, and the oxime nitrogen determined by a micro Kjeldhal. The large number of determinations which we made showed that the nitrogen content was always lower than that

calculated from the carbonyl groups as determined by titration. On an average, the ratio of carbonyl groups according to nitrogen determinations to carbonyl groups determined by titration amounted to 60-65% (Table 1).

We checked the accuracy of the nitrogen determinations in the cellulose-oximes by the Kjeldhal method by comparing the results with those of nitrogen determinations carried out by the Dumas method; good agreement was obtained.

Table 1

Deviation between content of carbonyl groups as determined volumetrically with $NH_2OH \cdot HCl$ in aqueous media, and as determined from the nitrogen content of the oximes formed (aqueous media pH 5-6)

No. of test	Carbonyl groups found		Ratio of carbonyl groups found by the nitrogen to that found by titration
	By titration (%)	By nitrogen (%)	
1	0.33	0.23	
	0.33	0.23	69
2	0.34	0.28	
	0.36	0.30	82
3	0.54	0.34	
	0.53	0.32	62
4	0.44	0.30	
	0.46	0.32	68
5	0.30	0.17	
	0.28	0.18	62

Table 2

Determination of carbonyl groups in hydroxycelluloses at a pH of 5-6 in alcohol media

No. of preparation	Carbonyl groups found		Ratio of carbonyl groups by nitrogen and by titration in %
	By titration (%)	By nitrogen (%)	
2	0.35	0.34	
	0.37	0.35	94
3	0.55	0.45	
	0.57	0.45	82
4	0.46	0.42	
	0.44	0.43	95
5	0.30	0.27	
	0.25	0.26	93

The disagreement between the amount of carbonyl groups as determined by titration and as determined by the nitrogen content may be the result of instability on the part of the oximes or of the nitrogen-containing groups in the hydroxycellulose in aqueous media, or the solubility of low molecular weight oxidation fractions of cellulose in water. A survey of the large number of experiments carried out under different conditions leads one to the conclusion that the reason for the disagreement in the analytical results is the instability of the hydroxamic derivative of the hydroxycellulose. The following facts seem to favor this hypothesis. Carbonyl groups and nitrogen were determined, respectively, in hydroxycellulose which was known to contain no lactone bonds after preliminary treatment with dilute alkali. In this hydroxycellulose, the percentage of carbonyl groups as determined by the titration method (0.18%) was close to that found from nitrogen determinations (0.20%). In the absence of lactone groups, therefore, both methods give results in good agreement.

It was shown that when condensation with hydroxylamine was carried out in an alcohol medium at a pH of 5-6 (Table 2), the titration results approximated to nitrogen determination results. Under these conditions both the carbonyl as well as

some of the lactone groups react, but no nitrogen of the hydroxycellulose oxime is lost. As a result, the hydroxamic derivatives of the hydroxycellulose which are broken down during water washing are stable in alcoholic media.

Results of condensation in alcoholic media at lower pH's also practically coincide, but the absolute values are lower than in the preceding case since in this case only carbonyl groups undergo condensation (Table 3).

When condensation is carried out at a pH of 3-4 there is no need for a preliminary neutralization of the carboxyl groups of the hydroxycellulose by treating with calcium acetate, since the extent of the dissociation of the COOH- groups at this pH in an alcoholic medium is insignificant. From work on the determination of carbonyl groups in low molecular weight compounds, it is known that in an alcoholic medium at a pH of 2.5 the presence of organic acids does not affect the accuracy of the determination [6]. We confirmed this in the case of hydroxycellulose, by carrying out parallel experiments on the determination of carbonyl groups in the same preparation with and without neutralization of the COOH groups (Table 4).

Results of comparative determinations of carbonyl groups by two methods the hydroxylamine method of Gladding and the specific method which we have put forward are given in Table 5. Values for the carbonyl group content as determined from oxime nitrogen are also given in the Table.

Table 3

Determination of carbonyl groups in hydroxycelluloses at a pH of 3-4 in alcoholic media

No. of preparation	Carbonyl groups found		Ratio of carbonyl groups by nitrogen and by titration
	By titration (%)	By nitrogen (%)	
1	0.26	0.23	91
	0.25	0.23	
2	0.31	0.26	86
	0.30	0.27	
3	0.29	0.29	100
	0.30	0.29	
4	0.29	0.25	96
	0.26	0.26	
5	0.20	0.20	100
	9.21	0.20	

Table 4

Determination of carbonyl groups in alcohol media at different pH values without preliminary neutralization of the hydroxycellulose, and after neutralization

No. of preparation	Carboryl groups found, pH 3-4, alcoholic media		Carbonyl groups found pH 5-6 alcoholic media	
	Without neutralization	After neutralization	Without neutralization	After neutralization
1	0.26	0.23	0.51	0.33
2	0.30	0.28	0.68	0.36

The results given in Table 5 show that the values found for the carbonyl groups by titration according to our specific method are less than the values found by Gladding's method as a result of the exclusion of reactions involving lactone groups. At the same time they are very near to the values found via nitrogen determinations.

Thus, an experimental check on Gladding s method has shown that this method gives results for the carbonyl groups which are too high in the case of hydroxycelluloses produced by hypochlorite oxidation; it thereby gives values which are too high for the keto-groups when the keto groups are determined from the difference between total percentage of carbonyl groups and percentage of aldehyde groups. All hydroxycelluloses containing lactone bonds will give this error. The true percentage of carbonyl groups in the presence of lactone groups can be obtained if the analysis is carried out under

the conditions described in the present article.

TABLE 5

Determination of carbonyl groups in hydroxycelluloses by various methods

Preparation.	pH	Carbonyl groups found by titration (%)		Carbonyl groups found by nitrogen (%)	
		Gladding's method	Our method	Gladding's method	Our method
Oxidized with NaClO	4.6	0.33	0.25	0.23	0.23
Ditto	7	0.35	0.27	0.29	0.26
Ditto	4.0	0.53	0.29	0.33	0.29
Ditto	6.5	0.44	0.28	0 31	0.26
Ditto	9	0.29	0.20	0.18	0.20

Description of Analytical Procedure

Reagent solution is prepared as follows: 5 g of hydroxylamine hydrochloride is dissolved in 240 ml of 96% ethyl alcohol + 5 ml of water + 6 ml of a 0.2% alcoholic solution of bromophenol blue. To the yellow solution obtained is added 0.2 N NaOH dropwise until a color which differs according to which way it is viewed is developed (green in transmitted light and red in reflected light). The pH of the reagent should be within the limits 3.2 - 3.4, and this is checked potentiometrically. The reagent solution is freshly prepared before each determination. 2-3 g of hydroxycellulose is added to 60 ml of reagent and allowed to stand at room temperature for 2 hours. After the 2 hours the hydroxycellulose is filtered off and 50 ml of filtrate taken for titration. The hydrochloric acid liberated on condensations is titrated with 0.1 N NaOH till the two-color solution is obtained as before. Titration is carried out more accurately potentiometrically to a pH of 3.2. From the amount of 0.1 N NaOH used for titration, the percentage of carbonyl groups in the aliquot of hydroxycellulose taken can then be calculated by means of the formula:

$$x = \frac{a \cdot 0.0028 \cdot 1.2 \cdot 100}{\text{weight taken in g}}$$

where a is the amount of 0.1 N NaOH used for titration, in ml.

SUMMARY

1. The method described in the literature for the determination of carbonyl groups in hydroxycellulose, and which is based on condensation of the groups with hydroxylamine hydrochloride, gives results which are too high, as a result of the presence of lactone groups in the hydroxycellulose, which form hydroxamic acids with $NH_2OH \cdot HCl$.

2. Condensation of lactone groups with $NH_2OH \cdot HCl$ can be excluded by lowering the pH from 5-6 to 3-4 and simultaneously changing over from an aqueous to an alcoholic medium. Under these conditions only the carbonyl groups react.

3. The use of a more acid alcoholic medium decreases the degree of dissociation of the carboxyl groups in hydroxycellulose to such an extent that neutralization with calcium acetate before a determination is unnecessary. Neutralization of carboxyl

groups is essential only when there is a high percentage of COOH groups, e.g., in cellulose oxidized with nitrogen peroxide.

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THE PERSULFATE-COBALT METHOD OF DETERMINING MANGANESE AND CHROMIUM IN STEELS AND CASTS IN THE SAME ALIQUOT

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Recently several attempts have been made to work out a persulfate method for the determination of manganese in ferrous and non-ferrous metals in which silver is replaced by other, less expensive catalysts. Thus, mercuric nitrate has been suggested as a catalyst (cobalt and chromium interfere in this determination). Kuznetsov and Budanova [1], have proposed cobalt sulfate as a catalyst, either on its own or with nickel sulfate or cupric sulfate. This last method is of considerable interest, particularly for factory laboratories, and in this connection we have subjected their method to a detailed check under the conditions of a factory laboratory for a series of determinations.[1])

As a result of these tests it was established that:

1. Kuznetsov and Budanova's method is applicable to the determination of manganese in all the alloys tested: low and high alloy steels, casts, magnesium and aluminum alloys.
2. Of the three catalysts proposed by these authors the best results are given by the cobalt-nickel and cobalt-copper ones. The cobalt catalysts give somewhat lower results (of the order of 0.02 - 0.03%), which is obviously determined by some difficulty in determining the end point or by incomplete oxidation of the manganese.
3. There is no difference in the time taken to carry out analysis with silver as a catalyst or with the substitutes as catalysts.
4. For the analysis of simple or low alloy steels the amount of sample taken is 0.5 g while for casts the amount required is 0.2 g. Half the amount of persulfate stipulated in the recommended method is then sufficient for oxidation of the manganese in routine analysis.
5. Simple and low alloy steels can be dissolved in sulfuric acid (1:3) and they can be subsequently oxidized with a few drops of concentrated nitric acid.
6. Deviations from Kuznetsov and Budanova's method in the use of excess acid for dissolving the aliquot leads to low results. Oxidation of manganese by persulfate solution should only be carried out during boiling; addition of oxidizing agent to a solution which is not boiling leads to low results.
7. The undoubted advantages of the persulfate-cobalt method for determining manganese as compared with the persulfate-silver method recommend its wide use in factory and research laboratories.

Results are given below of the analysis of a number of metals by the persulfate-cobalt method (cobalt-nickel or cobalt-copper catalysts).

1) Assistant A. G. Kovaleva also participated in checking the method.

Table 1

Results of the determination of manganese in several metal samples by the persulfate-cobalt and persulfate-silver methods

No.	No. of sample	Manganese % by $AgNO_3$ method	Manganese by the persulfate-cobalt method
1	Normal 6-a	1.18	1.18; 1.16; 1.18; 1.17; 1.18
2	Normal 286	0.40	0.40; 0.40; 0.40; 0.40
3	Normal 124	0.57	0.57; 0.56
4	Normal 83	0.61	0.60
5	Cast-alloy	0.83	0.83; 0.83; 0.82; 0.80; 0.81; 0.81; 0.82; 0.83[1])
6	Simple steel	0.59	0.59; 0.61; 0.60; 0.60; 0.61; 0.59 0.59[2])
7	Cast 1331	0.74	0.73; 0.73
8	Cast 1332	0.71	0.71; 0.71
9	Steel 20-X	0.66	0.66; 0.66
10	Steel 20-X	0.63	0.63; 0.63
11	Forged piece 1404 I	0.63	0.61
12	Forged piece 1404 II	0.69	0.68
13	Forged piece 1398 I	0.62	0.61
14	Forged piece 1398 II	0.60	0.58
15	Forged piece 1370	0.68	0.68; 0.68
16	Forged piece 1412	0.62	0.60
17	Duralumin S.O. 69	0.69	0.70; 0.71
18	Magnesium Alloy	0.25	0.23; 0.24

During a study of the persulfate-cobalt method of determining maganese it was found that this method is also applicable to the determination of chromium immediately after determining the manganese.

Simultaneous determination of manganese and chromium on one aliquot of cast iron or steel doubles the speed of analysis and leads to a considerable saving in reagents. Such a method is particularly useful in express analysis or during smelting.[3])

This method consists essentially of the oxidation of chromium with a persulfate solution in the presence of a cobalt-copper or cobalt-nickel catalyst to bichromate; after the manganese has been determined by the arsenite method, the

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1) The other nine results are the same, and equal to 0.83%.

2) The other six results which are not enumerated are all 0.59%.

3) The simultaneous determination of chromium and manganese by the persulfate silver method on one aliquot has already been adopted in the chemical laboratory of the "Hammer and Sickle" factory at the instigation of Chemical Engineers Simakina and Grigoreva.

bichromate is titrated with Mohr's salt in the presence of phenylanthranilic acid.

This method is applicable to steels containing up to 1.5% chromium. When the method described below was used, the results given in Table 2 were obtained.

These results show that the deviation between the method accepted at present and the method which we propose is within the limits of experimental error.

Table 2

Results of comparative determinations of chromium by the persulfate-silver and by the method suggested

No. in order	Sample Designation	Chromium % found by persulfate-silver method	Chromium % found by persulfate-cobalt method
1	Forged piece 50	0.94	0.92; 0.92
2	Forged piece 50-a	0.96	0.94; 0.96
3	Normal	1.56	1.53; 1.56
4	Forged piece 1382 I	0.95	0.94
5	Forged piece 1382 II	0.95	0.94
6	Forged piece 1404 I	0.73	0.76
7	Forged piece 1404 II	0.85	0.87
8	Forged piece 1398 I	0.85	0.84
9	Forged piece 1398 II	0.87	0.88
10	Forged piece 1379 I	1.04	1.06
11	Forged piece 1412	0.94	0.96
12	Forged piece 1379 II	1.00	1.00

Experimental Procedure. 0.5 g of steel or 0.2 g of cast is dissolved in 25 ml sulfuric acid (1.3), and oxidized with a few drops of concentrated nitric acid. The solution is heated until all the nitrogen oxides have been removed, when it is diluted with 150 ml of hot water, and 10 ml of the Kuznetsov-Budanova solution of cobalt-nickel or cobalt-copper catalyst immediately added (the cobalt-nickel catalyst is an aqueous solution containing 0.5% $CoSO_4 \cdot 7H_2O$ and 1.5% $NiSO_4 \cdot 7H_2O$; while the cobalt-copper catalyst is an aqueous solution containing 0.5% $CoSO_4 \cdot 7H_2O$ and 2% $CuSO_4 \cdot 5H_2O$). The mixture is brought to the boil. 15-20 ml 20% ammonium persulfate solution is carefully added to the boiling solution and the whole brought up to the boil again and boiled for 2-3 minutes. The solution is kept on a hot plate until the ammonium persulfate ceases to decompose when it is cooled in running water. 10 ml of sulfuric acid (1:3) is added to the solution which has been cooled to room temperature and the solution titrated with a solution of sodium arsenite[1]) to a change from violet to yellow (manganese determination). 4-5 drops of a phenylanthranilic acid solution is immediately added to the yellow solution (0.2 g of the acid is dissolved in 100 ml of boiling water containing 0.2 g sodium carbonate). After 1 minute the solution which is now a violet-wine color is titrated with a solution of Mohr's salt to a green end point (chromium determination).

The time taken for a chromium determination after titration of permanganate is not more than 3 minutes.

The method described in the present article is being used in a number of metallurgical and metal working factories.

1) In this case an arsenite nitrite mixture cannot be used for titration because the nitrites destroyed thereupon react with the phenylanthranilic acid.

SUMMARY

1. The Kuznetsov-Budanova method for the determination of manganese in ferrous and non-ferrous metals by means of a persulfate-cobalt catalyst has been checked.

2. It has been found that this method can completely replace the persulfate-silver method of determining manganese and can be recommended for wide practical application.

3. Using this method as a basis, another one has been developed for the simultaneous determination of manganese and chromium on one aliquot of steel or cast.

4. The method worked out is finding application in factory laboratories.

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HISTORY OF THE DEVELOPMENT OF ANALYTICAL CHEMISTRY IN RUSSIA. A RATIONAL METHOD OF CHECKING THE COMPOSITION OF A COMPOUND FROM ANALYTICAL RESULTS PROPOSED BY P. EINBRODT

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About 100 years ago Pavel Einbrodt, the Professor of Chemistry at Kharkov State University, published an interesting paper [1], under the title " Concerning the arithmetic control of analysis and the formula deduced on the basis of the analysis" . In this article he pointed out that in the usual method of comparing the percentage composition found with the calculated value, the difference between the experimental and theoretical amount of a given element leads to an error which is inversely proportional to the atomic weight of this element, since in the course of the subsequent determination of the number of atoms of this element in the formula, its percentage content is divided by the atomic weight.

He observed further that an error in the determination of one of the elements leads to a smaller error in the indirect determination of any other element in the same compound, the greater the number of atoms of this second element contained in the compound.

Einbrodt emphasized that these considerations have a special significance for the analytical control of the formulas of organic compounds.

In order to increase the accuracy of calculation he proposed that the content of each element be divided by the product of the number of its atoms and its atomic weight, and then to compare these coefficients with one another and with a "normal coefficient" which he calculated from the formula $Q_i = 100/M_i$, where M_i is the molecular weight corresponding to the i'th formula chosen for the given compound.

From this it is clear that the coefficient for each k'th element comprising the i'th formula of the given compound is determined by the expression:

$$q_{ik} = \frac{100W_k}{n_{ik}A_k} \qquad (1)$$

where W_k- is the amount of the k'th element determined experimentally in 1 g of material: n_{ik} the number of atoms of the k 'th element in the analytically checked i'th formula; A_k- the atomic weight of the k'th element.

Einbrodt affirmed that "if both formula and analysis are correct, then all the coefficients should be the same" , i. e. each of the values of q_{ik} should coincide with the normal coefficient Q_i. This statement is correct since from the very definition of the value of W_k it is obvious that

$$W_k = \frac{n_{ik}A_k}{\sum_{k=1}^{p} n_{ik}A_k} = \frac{n_{ik}A_k}{M_i}, \qquad (2)$$

where p- is the number of all the elements making up the given compound.

On the other hand, as Einbrodt writes, "any error in the correct formula - in the determination of the amount of an element, or in the formula derived - as the result of a correct analysis should appear as differences in the coefficients obtained (q_{ik}) both among themselves and also with respect to the normal coefficient Q_i".

Einbrodt applied his method for checking the formulas of chloroacetic acid and meconic acid suggested by Dumas, Lowig, and Liebig. From the tables adduced in his work it is obvious that all these formulas should be rejected because the coefficients found differ among themselves fairly considerably. Einbrodt, however, refrained from drawing a categorical conclusion and endeavored to justify the discrepancies found on the basis of analytical errors and the purity of the materials. Einbrodt did not pay attention to the fact that his method could be used so as to correct the formula if it had been chosen incorrectly, so that the molecular weight of the test material could be evaluated.

Einbrodt's contemporaries were unable to use or appreciate his method since only a very few of the formulas in use at that time, as listed in Berzelius's book [2] were correct. Up to the time when Butlerov's structural theory appeared, Einbrodt's method, which anticipated his contemporaries' potentialities, was finally forgotten, and as a result chemists who establish the formula of compounds from analytical results, even now use methods which Einbrodt correctly criticized 100 years ago

It is clear to us that Soviet chemists should turn their attention to Einbrodt's forgotten method and use it widely in their work. Below we have given some examples of the calculations involved in Einbrodt's method so as to illustrate its possibilities. In these examples we used the more convenient coefficients $M_i/M_i = 1$ for each compound instead of Einbrodt's normal coefficient which is equal to $100/M_i$. The calculations themselves are, where necessary, supplemented by mathematical statistical methods, which enhance the value of Einbrodt's method even more.

As our first example we have considered the choice of formula for papaverine which as is known [3], was not established immediately, since the formula accepted nowadays viz. $C_{20}H_{21}O_4N$ and which was proposed as long ago as 1848 by Merck was regarded as incorrect for a long time, and the formula $C_{21}H_{21}O_4N$ was put forward in its place by Hess in 1870.

Let us assume that as a result of one combustion it was established that papaverine contains C-70.90% and H-6.21%, while analysis for nitrogen gave N-4.16%. In this case the oxygen content by difference will be 18.73%. In Table 1 these results are initially used for calculating the coefficients q_{ik} corresponding to Hess' formula. It is clear from Table 1 that the coefficient for carbon differs appreciably from all the other remaining values of q_{ik} which are considerably greater than unity. A normal comparison of the mean of the three q_{ik}'s which are greater than unity, with the value 0.988 [4], shows that the differences between them cannot be explained by random errors, since the probability of a value $t_1 = 10.2$ as a result of random errors for a number of degrees of freedom $k = 2$ is less than 0.027 [5]. In so far as all the values of q_{ik} differ from unity by more than 1%, it is obvious that this deviation is connected with an incorrect choice of formula, since the determinations of individual elements in elemental analysis can scarcely include errors of more than 0.5%. Further comparison of the values of q_{ik} shows that the values of q for H, N, and O are practically the same; from which it follows that the indices for the symbols H, O, and N in the formula $C_{21}H_{21}O_4N$ are correct, while the index for C contains an error, with a consequent error in the molecular weight.

In order to find the correct value of the molecular weight M_x formula (3) can be used

$$M_x = \frac{n_{ik} A_k}{W_k}, \qquad (3)$$

which is easily derived from formula (2), if 100 is put instead of M_i and it is taken into account that $q_{ik} = 1$ for such a substitution. It was in this way that the values of M_x adduced in Table 1 were derived; the mean value of $\bar{M}_x = 339.7$ is less than the molecular weight corresponding to Hess' formula by 11.7, i.e., by an amount approximately equal to the atomic weight of carbon. This confirms the correctness of the formula $C_{20}H_{21}O_4N$, as is also proved by the values of q_{ik} given in the last column of Table 1.

Table 1

Application of Einbrodt's method for choosing the formula of papaverine

			Hess' formula $C_{21}H_{21}O_4N$ M = 351.4				Merck's formula $C_{20}H_{21}O_4N$ M = 339.4	
	W_k	A_k	n_{ik}	q_{ik}	$q_{ik} > 1$	M_x	n_{ik}	q_{ik}
C	0.7090	12.010	21	0.988	—	—	20	1.002
H	0.0621	1.008	21	1.032	1.032	340.7	21	0.996
N	0.0416	14.008	1	1.044	1.044	336.7	1	1.008
O	0.1873	16.000	4	1.029	1.029	341.7	4	0.993
		Mean		1.023	1.035	339.7		0.9998

$s^2 = 4.2 \cdot 10^{-5}$; $s = 4.6 \cdot 10^{-3}$; $t = \frac{1.035 \quad 0.988}{4.6 \cdot 10^{-3}} =$

$= 10.2$; $P(|t| \geqslant 10.2) < 0.027$; $351.4 - \bar{M}_x = 11.7 \sim 12$

Table 2

Application of Einbrodt's method for choosing the formula of bromphenolblue

			$C_{19}H_{12}O_6Br_4S$ M = 688.0				$C_{19}H_{10}O_5Br_4S$ M = 670.0	
	W_k	A	n_{ik}	q_{ik}	$q_{ik} > 1$	M_x	n_{ik}	q_{ik}
Br	0.4775	79.916	4	1.028	1.028	669.5	4	1.001
S	0.0476	32.06	1	1.022	1.025	673.5	1	0.995
		Mean		1.025		671.5		0.998

$688.0 - \bar{M}_x = 16.5 \sim 18$

Normally, in order to determine the formula of a compound, analysis is confined to the determination of one or two elements. In those cases where the molecular weight of a compound is established by independent determinations, it is obvious that any n_{ik} can be calculated by means of equation (3). In those cases where the correct value of M is unknown, one must resort to the methods shown in Table 1. As an example we shall consider Orndorff and Sherwood's analysis [6],

on the basis of which they concluded that bromophenolblue is a sulfonphthalein and not a sulfonic acid. Results for bromine and sulfur, which were found to be 47.75 and 4.76, respectively, were used in Table 2. From this table it is clear that the values of q_{ik} correspond to the formula of a sulfonic acid and are approximately equal, but are greater than 1 by more than 2%; such a deviation cannot be explained by random errors. The values of M_x, calculated by means of formula (3) are very near to the molecular weight corresponding to a sulfonphthalein. The values of q_{ik} correspond to the formula $C_{19}H_{10}O_5Br_4S$ and are very nearly one.

These examples are enough to recommend Einbrodt's method for wider application.

SUMMARY

1. A rational method which was proposed 100 years ago by P. Einbrodt, Professor of Chemistry at Kharkov University, for checking th composition of a compound from analytical results has been described.
2. Examples are given of the application of this method under present day conditions.

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[1)] See Consultants Bureau Translation, page 361.

IVAN PAVLOVICH ALIMARIN

(On the occasion of his fiftieth birthday)

In August, 1953, Professor Ivan Pavlovich Alimarin, one of the foremost analytical chemists of our country and a doctor of chemical sciences celebrated his fiftieth birthday and 30 years of scientific and teaching activity.

All his many-sided activities have been devoted by Alimarin to scientific-teaching and scientific-organization work connected with the development of analytical chemistry in Russia.

Alimarin, while still a youngster of 16, on the advice of his teacher, Prof. K. I. Viskonta, started to work at the Plekhanov Institute of National Economy in the Student's faculty on practical inorganic chemistry. He devoted all his spare time enthusiastically to experiments in analytical chemistry.

In 1928 Alimarin started to work as an assistant in the Mineralogical section of Moscow State University, from which he proceeded to the M. V. Lomonosov Institute of Fine Chemical Technology as a lecturer, and, ultimately, from 1948-1953 was professor at the head of the analytical chemistry section.

Since April 1953 he has been the head of the chair of analytical chemistry in Moscow State University.

A new stage in Alimarin's life was reached when he started to work (1923) in the Institute of Applied Mineralogy (at present VIMS). In this institute, where he worked for 30 years, he personally carried out hundreds of complex analyses of mineral raw materials and developed new analytical methods. Initially he worked as a scientific coworker, but subsequently became head of the analytical laboratory, and in this work he became an outstanding analytical chemist. From 1949 he headed the laboratory of Microchemistry in the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry.

In the course of more than 30 years, Alimarin combined both scientific and teaching activity, and his fruitful activity shows him to be one of the foremost specialists in the field of analytical chemistry.

His scientific activity is distinguished by its wide variety; either on his own or in conjunction with other workers he has carried out about 200 researches. The basis of all this work was indissolubly related to the problems of improving the national economy.

The field in which he may be regarded to have specialized in mainly is that of analysis of small amounts of material.

He studied the distribution of rare elements in minerals, as a result of which he has produced new analytical methods. He also carried out work on the chemical concentration of the rare elements. As a result of this work, which extended over the course of many years, he proposed new methods of concentrating and quantitatively determining the following elements: Nb, Ta, Zr, V Ge, Re, In, Te, Ga, Li, etc.

Of particular interest are the methods of isolating and determining Nb, Ta, and Ge, which find manifold uses in Russian laboratories.

The most recent investigations of Alimarin and his coworkers have been along the lines of developing new physico-chemical methods (colorimetry, polaro-

graphy, amperometry), for scattered elements. New methods have been developed or old ones improved; colorimetric determination of V, Nb, Te, Cr, Si, polarographic determination of Sn, Ge, Cr, V and an amperometric titration of Fe, Cr, V.

He has also adopted the methods of micro- and ultra-micro- methods of analysis, a logical development, since he has always been interested in the chemistry of small amounts.

Alimarin has also developed special methods and apparatus for use in geological prospecting which have found wide application.

As a result of his work along these lines, a technique of microanalysis of silicate minerals and ores has been perfected. Moreover, in conjunction with B. Frid he has written a monograph on "A practical textbook on the microanalysis of minerals and ores".

A second edition of "Qualitative Semi-microanalysis" by I. P. Alimarin and V. N. Arkhangelskaya, which has been successfully used in University courses in qualitative analysis, has recently come out.

In search of new and better analytical methods, Alimarin has done a lot of theoretical work on the study of the mechanisms of analytical reactions, which occur during the formation of precipitates and complex compounds. The study of the structure of precipitates formed during analysis, of the complex compounds of niobium and tantalum, and of the reactions of several of the rare elements in lower oxidation states belong to this category.

Alimarin has widely used the periodic law of Mendeleev in his work. Using this law during a study of analogous analytical properties of the elements in relation to their position in the periodic system, he has worked out the following new, original reactions: the formation of a heteropolyacid of germanium and its compound with orthohydroxyquinoline; the precipitation of niobium and tantalum with phenyl arsenic acid, the interaction of niobium with thiocyanic acid, thymol, guaiacol, and hydroxyanthraquinone.

Alimarin has devoted a lot of attention to the state of an element in solution (ions, molecules, colloidal particles) and to the step-wise process of reaction in solutions.

What has already been said does not by any means exhaust the work carried out by Alimarin.

In the course of many years his activity has been characterized by the fact that his most important researches and his newest achievements in the field of analytical chemistry have been reflected in his teaching work. It is his wish to communicate to his students his own experience and also the classical methods of analysis. At the same time he tries to inculcate in them a spirit of alertness and accuracy in their work. He pays a great deal of attention to the work of his students and to the theses of candidates for the doctor and master's degree, as well as a consultant to workers in factory laboratories.

His coworkers, and those working under his direction, value his work and successfully apply his experience in chemical analysis. Purposefulness, vigor, and a polished style of work are characteristic of Alimarin's students.

Alimarin participates fully in the various All-Union conferences on analytical chemistry, on the editorial board of State Chem. Press and in the J. Anal. Chem., and also in the chemical section of VAK.

For his work he has been rewarded by the Soviet Government.

In 1944 he was awarded the Order of the Red Star, and in 1953 was awarded the Order of Lenin.

In noting that today Alimarin celebrates both his fiftieth birthday and 30 years of scientific-teaching activity, his comrades, coworkers, and a wide circle of Soviet analytical chemists will send him their sincerest wishes for his health and for his fruitful work for the good of Russia.

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